

Chapter 1: Zeroth law of thermodynamics and equation of state

Classical Thermodynamics

Jussi Eloranta (eloranta@aa6kj.hopto.org)

(Updated: November 5, 2020)

“Classical thermodynamics is a statistical model. It has no knowledge of individual atoms and molecules. It uses only macroscopic variables such as temperature, pressure and volume for describing the system.”

4



William Thomson, Irish-Scottish physicist and mathematician (“Lord Kelvin”; 1824 – 1907): *Absolute temperature scale* (1848). One of the most important contributors to the 19th century physical sciences.

A diagram illustrating the concept of a thermodynamic system. A central white circle is labeled "System". It is surrounded by a light blue area labeled "Surroundings". A black line separates the system from the surroundings, with an arrow pointing to it from the label "Boundary". A curved arrow points from the system into the surroundings, representing energy transfer.

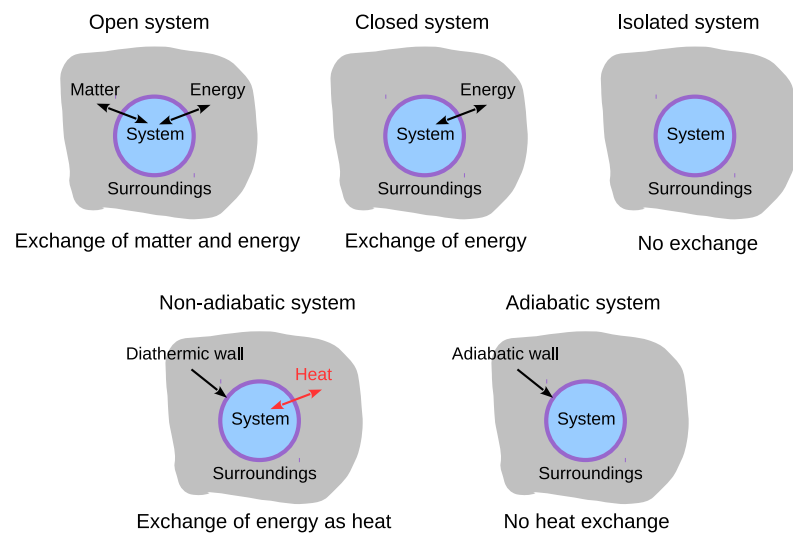
System: single molecule, solid, gas, liquid, etc.

Surroundings: solvent, container, gas cylinder, etc.

Boundary: Interaction between the system and the surroundings (forces between atoms and molecules) or vacuum (no interaction).

“Focus on the system and treat the surroundings approximately”

Non-isolated system	Interaction with the surroundings.
Isolated system	No interaction with the surrounding.
Open system	Exchange of matter/energy with the surroundings.
Closed system	No exchange of matter/energy.
Adiabatic system	No exchange of heat with the surroundings.
Heterogeneous system	Multiple phases in the system.
Homogeneous system	Single phase system.



Phase

Thermodynamic variables

Extensive variable

Intensive variable

Intensive state

Extensive state

Equilibrium

Solid, liquid or gas (heterogeneous, e.g. water with ice).

Variables that specify the state of the system.

(for example P , T , V) (or state variables).

Variable depends on the size of the system.

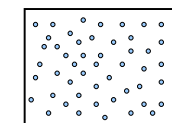
Variable does not depend on the size of the system.

System variables that are intensive.

System variables that are extensive.

System does not change as a function of time.

The most common variables are P (Pressure), V (Volume), n (amount of substance) and T (Temperature). When n is fixed, two variables need to be specified for a single phase system. Why is thermodynamic description needed?



Microscopic view
Individual atoms and molecules



Macroscopic view
distribution of atoms and molecules

Microscopic definition of a system requires typically large number of variables. One mole of gas molecules would mean more than 6×10^{23} variables!

Molar volume is defined as the ratio between volume V (m^3 or $\text{dm}^3 = \text{L}$) and the number of particles in it n (mol):

$$\bar{V} = \frac{V}{n} \quad (1.1)$$

The amount of substance n (mol) is given by:

$$n = \frac{N}{N_A} = \frac{N}{6.022 \times 10^{23} \text{ mol}^{-1}} = \text{“moles of substance”} \quad (1.2)$$

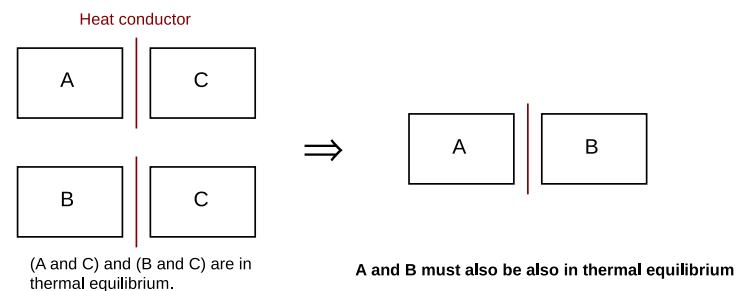
where N is the number of molecules.

Use SI-units in all calculations. Convert to other units at the final stage.

At equilibrium a system is described by its thermodynamic variables. *Thermodynamic equation of state* introduces dependencies between the variables. An example of thermodynamic equation of state is the ideal gas law ($PV = nRT$), which allows to express any of the five variables as a function of the remaining ones.

1.2 The zeroth law of thermodynamics

Thermal equilibrium between two systems means that they have been in thermal contact for sufficiently long time so that they have the same temperature. The following transitivity rule is called the *zeroth law of thermodynamics*:



According to our every day knowledge of thermal objects, this law appears quite natural. Formally, it is needed for defining the temperature scale. The zeroth law of thermodynamics does not have any “direct” applications but it is needed for making thermodynamics a complete theory.

Given that n is fixed and P is small, experimental results have established the Boyle's law:

$$PV \approx \text{constant} \quad (1.3)$$

Furthermore experiments have shown that under the same conditions (Charles & Gay-Lussac), PV is proportional to temperature:

$$PV \propto T \quad (1.4)$$

To formally define a temperature scale, we use the guidance provided by these experimental observations. For a system in two different states (P_1, V_1 and P_2, V_2), their relative temperatures are defined as:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2} \quad (1.5)$$

Note that this definition of temperature ("ideal gas temperature") is valid only in the limit of zero pressure. These results also suggests the ideal gas law:

$$PV = nRT \quad (1.6)$$

where proportionality constants n and R correspond to the amount of gas (mol) and the molar gas constant (8.31451 J / (mol K)), respectively.

1.3 The ideal gas temperature scale

Following the ideas of the previous section, we define the ideal gas temperature:

$$T = \lim_{P \rightarrow 0} \frac{P\bar{V}}{R} = \lim_{P \rightarrow 0} \frac{PV}{nR} \quad (1.7)$$

The unit of thermodynamical temperature is Kelvin (1 / 273.16 of the temperature of the triple point of water). Conversion between different temperature units:

$$t = T - 273.15 \text{ (Celsius degrees } (t) \text{ and Kelvin degrees } (T)) \quad (1.8)$$

$$t = \frac{9}{5} (T - 273.15) + 32 \text{ (Fahrenheit degrees } (t) \text{ and Kelvin degrees } (T)) \quad (1.9)$$

Also note that the SI unit of pressure P is pascal (Pa; N / m²). The atmospheric pressure is 101,325 Pa. Other units of pressure are atmospheres (atm) and bar.

Overview of basic SI units

SI units are an international standard (MKS; 1960).

Quantity	Unit	Symbol	Definition
length	meter	m	Fixed to speed of light.
mass	kilogram	kg	Weight of a reference cylinder.
time	second	s	Fixed to Cs radiative lifetime.
current	ampere	A	Fixed to current in reference system
temperature	kelvin	K	0 K = absolute zero, 273.16 K = triple point of H ₂ O.
luminous intensity	candela	cd	Fixed to a black-body reference.
amount of substance	mole	mol	The number of ¹² C atoms in 0.012 kg. Avogadro's constant gives the number of molecules in one mole; $N_A = 6.022137 \times 10^{23} \text{ mol}^{-1}$.

Quantity	Unit	Symbol	Definition
force	newton	N	1 N = 1 kg m s ⁻²
energy	joule	J	1 J = 1 kg m ² s ⁻²
electric charge	coulomb	C	1 C = 1 As
pressure	pascal	Pa	1 Pa = 1 N m ⁻²
magnetic field	tesla	T	1 T = 1 kg s ⁻² A ⁻¹
frequency	hertz	Hz	1 Hz = 1 s ⁻¹
power	watt	W	1 W = 1 J s ⁻¹
voltage	volt	V	1 V = 1 W A ⁻¹
resistance	ohm	Ω	1 Ω = V A ⁻¹

Non-SI unit	SI unit	Conversion factor
ångström (Å)	meter (m)	1 Å = 10 ⁻¹⁰ m
inch (in)	meter (m)	1 in = 2.54 cm = 0.0254 m
foot (ft)	meter (m)	1 ft = 12 in = 0.3048 m
mile (mi)	meter (m)	1 mi = 5280 ft = 1609.344 m
AMU	kilogram (kg)	1 AMU = 1.66054 × 10 ⁻²⁷ kg
eV	joule (J)	1 eV = 1.602177 × 10 ⁻¹⁹ J
cal	joule (J)	1 cal = 4.1868 J
torr (Hgmm)	pascal (Pa)	1 torr = 1.33322 × 10 ² Pa
atmospheres (atm)	pascal (Pa)	1 atm = 1.01325 × 10 ⁵ Pa
bar	pascal (Pa)	1 bar = 10 ⁵ Pa
psi	pascal (Pa)	1 psi = 6.8948 × 10 ³ Pa
gauss (G)	tesla (T)	1 G = 10 ⁻⁴ T

Common conversion factors. In Kelvin units, the energy corresponds to kT . Note also that $1\text{ K} = 3.1669 \times 10^{-6}\text{ Hartree}$ (atomic units; a. u.) or $1\text{ eV} = 27.2114\text{ Hartree}$. To get J mol^{-1} or kcal mol^{-1} , multiply by Avogadro's number N_A . For example, $1\text{ eV} = 1.602177 \times 10^{-19}\text{ J}$ and $1\text{ atm} = 760\text{ torr}$.

Mass – Energy

kg	u	J	eV
1	6.022137×10^{26}	8.987552×10^{16}	5.609586×10^{35}
1.660540×10^{-27}	1	1.492419×10^{-10}	9.314943×10^8
1.112650×10^{-17}	6.700531×10^9	1	6.241506×10^{18}
1.782663×10^{-36}	1.073544×10^{-9}	1.602177×10^{-19}	1

Spectroscopic units

Hz	cm^{-1}	Ry	eV
1	3.335641×10^{-11}	3.039660×10^{-16}	4.135669×10^{-15}
$2.99792458 \times 10^{10}$	1	9.112671×10^{-6}	1.239842×10^{-4}
3.289842×10^{15}	1.097373×10^5	1	1.360570×10^1
2.417988×10^{14}	8.065541×10^3	7.349862×10^{-2}	1

Energy

K	kWh	kcal	J	eV
1	3.83516×10^{-30}	3.298×10^{-27}	1.38066×10^{-23}	8.61739×10^{-5}
2.60745×10^{29}	1	8.598×10^2	3.60000×10^6	2.24694×10^{25}
3.0325×10^{26}	1.1630×10^{-3}	1	4.1868×10^3	2.6132×10^{22}
7.24292×10^{22}	2.77778×10^{-7}	2.388×10^{-4}	1	6.241506×10^{18}
1.16045×10^4	4.45049×10^{-26}	3.827×10^{-23}	1.602177×10^{-19}	1

Pressure

Pa	bar	kp / cm^2	torr (mmHg)	atm
1	10^{-5}	1.020×10^{-5}	7.5006×10^{-3}	9.869×10^{-6}
10^5	1	1.020	7.5006×10^2	9.869×10^{-1}
9.807×10^4	9.807×10^{-1}	1	7.3556×10^2	9.678×10^{-1}
1.333×10^2	1.333×10^{-3}	1.360×10^{-3}	1	1.316×10^{-3}
1.013×10^5	1.013	1.033	760	1

1.4 Ideal mixtures and Dalton's law

Eq. (1.6) applies also to mixtures of ideal gases:

$$P = (n_1 + n_2 + \dots) \frac{RT}{V} = n_1 \frac{RT}{V} + \dots = P_1 + P_2 + \dots = \sum_i P_i \quad (1.10)$$

where n_i is the amount of species i (mol), $n = n_1 + n_2 + \dots$ is the total amount of gas (mol). and pressures P_i are partial pressures for species i (Pa). Thus the total pressure P is a sum of all partial pressures (Dalton's law). Each species obeys the ideal gas law also separately.

Partial pressure P_i can also be expressed using mole fractions (y_i). When RT/V is replaced by P/n in Eq. (1.10), we get:

$$P_i = \frac{n_i}{n} P = y_i P \quad (1.11)$$

Example. The mass percentage composition of dry air at sea level is approximately N₂:75.5, O₂:23.2 and Ar:1.3. What is the partial pressure of each component when the total pressure is one atmosphere (1.00 atm)?

Solution. First calculate the molar mass for each species:

$$m(\text{N}_2) = 2 \times 14.01 \text{ AMU} \times \left(1.661 \times 10^{-24} \frac{\text{g}}{\text{AMU}} \right) \times N_A = 28.02 \frac{\text{g}}{\text{mol}}$$

$$m(\text{O}_2) = 2 \times 16.00 \text{ AMU} \times \left(1.661 \times 10^{-24} \frac{\text{g}}{\text{AMU}} \right) \times N_A = 32.00 \frac{\text{g}}{\text{mol}}$$

$$m(\text{Ar}) = 39.95 \text{ AMU} \times \left(1.661 \times 10^{-24} \frac{\text{g}}{\text{AMU}} \right) \times N_A = 39.95 \frac{\text{g}}{\text{mol}}$$

Since the partial pressure does not depend on the amount of air, we can choose the amount of air to be 1.00 g. The number of molecules in the air sample can be calculated:

$$n(\text{N}_2) = \frac{(1.00 \text{ g}) \times 0.755}{28.02 \text{ g mol}^{-1}} = 0.0269 \text{ mol}$$

$$n(\text{O}_2) = \frac{(1.00 \text{ g}) \times 0.232}{32.00 \text{ g mol}^{-1}} = 0.00725 \text{ mol}$$

$$n(\text{Ar}) = \frac{(1.00 \text{ g}) \times 0.013}{39.95 \text{ g mol}^{-1}} = 0.00033 \text{ mol}$$

The total amount of gas (sum of the above components) is 0.0345 mol. The mole fractions and partial pressures are then:

	N ₂	O ₂	Ar
Mole fraction	0.780	0.210	0.0096
Partial pressure (atm)	0.780	0.210	0.0096

Note: The numerical values of the AMU to g conversion and N_A cancel in the calculation of m 's.

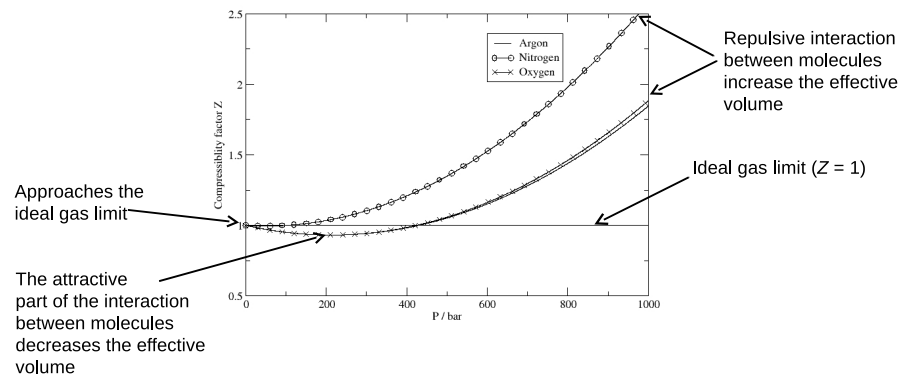
1.5 Real gases and the virial equation

17

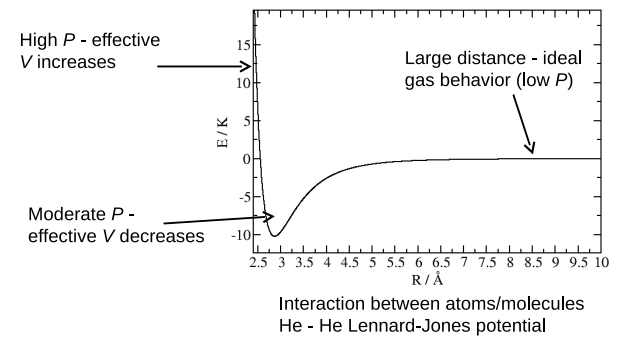
Real gases behave like ideal gases only in the limit of zero pressure and high temperature.

Compressibility factor Z indicates deviation from the ideal gas law:

$$Z = \frac{P\bar{V}}{RT} = \frac{PV}{nRT} \quad (1.12)$$



18



In the limit of high temperature, thermal energy dominates over the potential. At low temperatures the effect of the attractive part of the potential can be seen more clearly because thermal energy is not sufficient to smooth out the binding.

Note: The compressibility vs. pressure curves depend on the gas as well as the temperature.

A number of different equations of state for real gases have been proposed:

Ideal gas:
$$P = \frac{RT}{\bar{V}} \quad (1.13)$$

van der Waals (vdW):
$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad (1.14)$$

Berthelot:
$$P = \frac{RT}{\bar{V} - b} - \frac{a}{T\bar{V}^2} \quad (1.15)$$

Virial (Onnes):
$$P = \frac{RT}{\bar{V}} \left\{ 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \dots \right\} \quad (1.16)$$

Alternative forms of Eq. (1.16):

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \dots = 1 + B'(T)P + C'(T)P^2 + \dots \quad (1.17)$$



Kamerlingh Onnes, Dutch physicist (1853 – 1936),
Virial equation (1901),
Liquid helium (1908),
Nobel prize (1913).

where the relationship between the two constants are given by:

$$B'(T) = \frac{B(T)}{RT} \text{ and } C'(T) = \frac{C(T) - B(T)^2}{(RT)^2} \quad (1.18)$$

Note: Temperature where $B(T) = 0$ is called the Boyle temperature. At this temperature the gas behaves ideally over an extended range in pressure.

The above equations of state can be derived using statistical mechanics and assuming a certain type of pair interaction.

Example. Estimate the molar volume of CO₂ at 500 K and 100 atm by treating it as a van der Waals gas. For CO₂ the coefficients are: $a = 3.640 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 4.267 \times 10^{-2} \text{ L mol}^{-1}$.

Solution. First rearrange the van der Waals equation (Eq. (1.14)):

$$\bar{V}^3 - \left(b + \frac{RT}{P} \right) \bar{V}^2 + \left(\frac{a}{P} \right) \bar{V} - \frac{ab}{P} = 0$$

Roots of a cubic equation (molar volume is the unknown variable) can be found either analytically by using the appropriate formulas (by using the Maxima program described in the Appendix). Next, we setup numerical values for the coefficients:

$$b + RT/P = 0.453 \text{ L mol}^{-1}$$

$$a/P = 3.64 \times 10^{-2} (\text{L mol}^{-1})^2$$

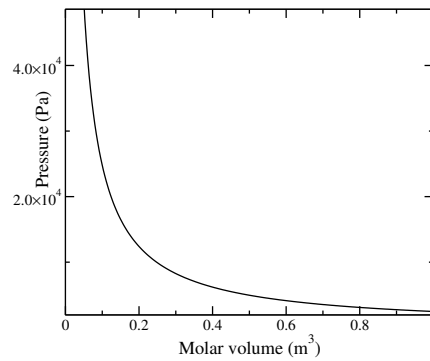
$$ab/P = 1.55 \times 10^{-3} (\text{L mol}^{-1})^3$$

Thus the equation is:

$$\bar{V}^3 - 0.453\bar{V}^2 + (3.64 \times 10^{-2}) \bar{V} - (1.55 \times 10^{-3}) = 0$$

The only real valued root is: $\bar{V} = 0.370 \text{ L mol}^{-1}$ (0.410 L mol^{-1} for ideal gas).

When the equation of state is given, it defines a surface in three dimensional space. The surface is such that it satisfies the equation state. This is difficult to visualize in 3-D and therefore 2-D projections are preferred (i.e., one variable is kept constant when plotting). An example is shown below where the temperature was held constant.



This example corresponds to an ideal gas at 298.15 K temperature. Such plots for other equations of state are shown in the following sections.

1.6 Critical phenomena

Definitions:

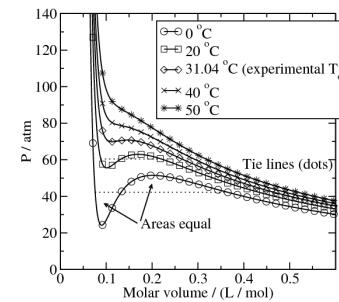
P_c = Critical pressure (the highest pressure where liquid can boil)

T_c = Critical temperature (the highest temperature where gas can condense)

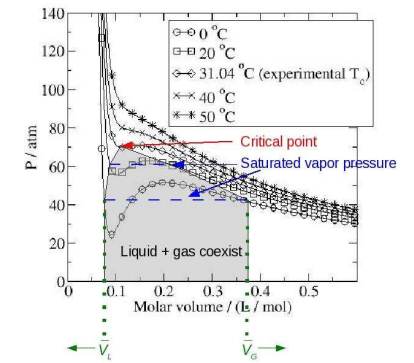
V_c = Critical volume (molar volume at the critical point)

Isotherm = $P\bar{V}$ curve that is obtained when temperature is held constant

Formally P_c , T_c and V_c define a region on the P - V - T surface where liquid and gas phase can coexist as two separate phases. Outside this region the phases cannot be separated.



Isotherms (Eq. (1.14) for CO_2).



Unphysical "loops" removed.

Note: The ends of tie lines indicate pure liquid (V_L) and pure gas phase (V_G) limits. When the tie line vanishes, V_G and V_L become identical and the phases cannot be distinguished from each other. Remember to stay on the isotherms when reading the above figures - states outside the isotherms are forbidden by the equation of state. In the last figure, the minima below the critical point have been replaced with a horizontal tie line.

Gas/liquid becomes supercritical above its critical point. In practice, a supercritical fluid has properties both of dense gas and low viscosity liquid. It can diffuse through materials like gas but it can dissolve materials like a liquid. Supercritical fluids are often used as substitutes for organic solvents (supercritical fluid extraction).

At the critical temperature the following conditions hold (inflection point):

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \quad (1.19)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0 \quad (1.20)$$

Isothermal compressibility is defined as (infinity at critical point):

$$\kappa = -\frac{1}{\bar{V}} \times \left(\frac{\partial \bar{V}}{\partial P}\right)_T \quad (1.21)$$

Terminology:

isothermal = Temperature does not change in the process.

adiabatic = No heat transfer in the process.

In addition to critical temperature, critical pressure (P_c) and critical volume (V_c) can also be defined by exchanging the roles of variables in Eqs. (1.19) and (1.20). Expressions for these quantities can be derived for various equations of state. For the van der Waals equation of state, we have:

$$P_c = \frac{a}{27b^2} \quad (1.22)$$

$$\bar{V}_c = 3b$$

$$T_c = \frac{8a}{27bR}$$

Exercise. Verify that the above expressions are correct. Use the van der Waals equation of state and Eqs. (1.19) and (1.20). Show that the following results hold for the Berthelot equation of state:

$$P_c = \frac{1}{6} \left(\frac{aR}{6b^3}\right)^{1/2} \quad (1.23)$$

$$\bar{V}_c = 3b$$

$$T_c = \frac{2}{3} \left(\frac{2a}{3bR}\right)^{1/2}$$

1.7 The van der Waals equation

Recall the van der Waals equation (Eq. (1.14)):

$$\underbrace{\left(P + \frac{a}{\bar{V}^2}\right)}_{P_{eff}} \underbrace{(\bar{V} - b)}_{\bar{V}_{eff}} = RT \quad (1.24)$$

This is similar to the ideal gas law but it uses effective pressure and volume. Reduction in the molar volume is needed because molecules have finite size (i.e. they are not point-like as assumed in the ideal gas law). This part is related to the repulsive wall of the molecule - molecule interaction. The effective pressure includes a correction that arises from attractive interactions between molecules (i.e. higher compressibility). Constants a and b depend on the gas. If monoatomic gas temperature is sufficiently high compared to its atom-atom binding energy, it can be shown that the parameters a and b are directly related to the atom - atom pair interaction $U_{12}(r)$ by (see Landau and Lifshitz, Statistical Physics Pt. 1):

$$a = \pi \int_{2r_0}^{\infty} |U_{12}(r)| r^2 dr \quad (1.25)$$

$$b = \frac{16}{3} \pi r_0^3$$

where parameter $2r_0$ denotes the point where $U_{12}(r)$ becomes repulsive (i.e. it becomes positive when the interaction at infinity is taken to be zero).



Johannes Diedrik van der Waals, Dutch physicist (1837 – 1923), Nobel prize (1910).

The compressibility factor Z for a van der Waals gas is given by:

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}} = \frac{1}{1 - b/\bar{V}} - \frac{a}{RT\bar{V}} \quad (1.26)$$

Taylor series. Function f that has derivatives of all orders can be expanded in Taylor series: $f(x) = a_0 + a_1(x - h) + a_2(x - h)^2 + a_3(x - h)^3 + \dots$ where the coefficients are given by:

$$a_0 = f(h) \text{ and } a_n = \frac{1}{n!} \left(\frac{d^n f(x)}{dx^n} \right) \Big|_{x=h} \quad (1.27)$$

and we say that the function was expanded about point h . When $h = 0$, the series expansion is called Maclaurin series.

Example. Find the Taylor series for $\ln(x)$, expanded about $x = 1$ (i.e. $h = 1$ above).

Solution. The first derivative of $\ln(x)$ is $1/x$, which equals 1 at $x = 1$. The second derivative is $-1/x^2$, which equals -1 at $x = 1$. The derivatives follow a regular pattern:

$$\left(\frac{d^n f}{dx^n} \right) = (-1)^{n-1} (n-1)!$$

so that we finally have: $\ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 - \frac{1}{4}(x-1)^4 + \dots$

When b/\bar{V} is small, we can use the Maclaurin series to expand:

$$\frac{1}{1-b/\bar{V}} = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \dots \quad (1.28)$$

Thus we can write the compressibility factor Z in Eq. (1.26) as (cf. Eq. (1.17)):

$$Z = 1 + \underbrace{\left(b - \frac{a}{RT}\right)}_{=B \text{ in Eq. (1.17)}} \frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \dots \quad (1.29)$$

Note that when T is small, $1/T$ is large and therefore a is important at low temperatures and b at high temperatures. The Boyle temperature can now be obtained from $B(T) = 0$ as:

$$T_B = \frac{a}{bR} \quad (1.30)$$

The following relations can be used to relate a, b and P_c, T_c, \bar{V}_c to each other:

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{9}{8}RT_c\bar{V}_c \Rightarrow T_c = \frac{8a}{9R\bar{V}_c} = \frac{8a}{27Rb} \text{ and } P_c = \frac{RT_c}{8b} = \frac{a}{27b^2} \quad (1.31)$$

$$b = \frac{RT_c}{8P_c} = \frac{\bar{V}_c}{3} \Rightarrow \bar{V}_c = 3b \quad (1.32)$$

Example. The experimentally determined critical constants for ethane are $P_c = 48.077$ atm and $T_c = 305.34$ K. Calculate the van der Waals parameters of the gas.

Solution. First convert everything to SI units:

$$P_c = 48.077 \times (1.013 \times 10^5) \text{ Pa} = 4.870 \times 10^6 \text{ Pa}$$

$$\bar{V}_c = 0.1480 \text{ dm}^3 \text{ mol}^{-1} = 14.80 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$T_c = 305.34 \text{ K}$$

Eqs. (1.31) and (1.32) allow to express a and b in terms of three different pairs (P_c, \bar{V}_c) , (T_c, \bar{V}_c) and (P_c, T_c) . The (P_c, T_c) pair is given here and hence the following form of equations should be used to get a and b :

$$a = \frac{27(RT_c)^2}{64P_c} \text{ and } b = \frac{RT_c}{8P_c} \quad (1.33)$$

$$\begin{aligned}
 a &= \frac{27 (RT_c)^2}{64 P_c} = \frac{27 \left(8.3145 \overbrace{\text{J}}^{\text{Nm}} \text{mol}^{-1} \text{K}^{-1} \times 305.34 \text{ K} \right)^2}{64 \left(4.870 \times 10^6 \underbrace{\text{Pa}}_{\text{Nm}^{-2}} \right)} = 0.5583 \frac{\text{Nm}^4}{\text{mol}^2} \\
 &= 0.5583 \frac{\left(\frac{\text{N}}{\text{m}^2} \right) \text{m}^6}{\text{mol}^2} = 0.5583 \frac{\text{Pa m}^6}{\text{mol}^2} = 0.5583 \frac{(9.869 \times 10^{-6} \text{ atm}) (10 \text{ dm})^6}{\text{mol}^2} \\
 &= 5.510 \text{ dm}^6 \text{ atm mol}^{-2} \\
 b &= \frac{RT_c}{8 P_c} = \frac{8.3145 \text{ J mol}^{-1} \text{K}^{-1} \times 305.34 \text{ K}}{8 \times (4.870 \times 10^6 \text{ Pa})} = 6.652 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \\
 &= 6.652 \times 10^{-5} \times (10 \text{ dm})^3 \text{ mol}^{-1} = 0.06652 \text{ dm}^3 \text{ mol}^{-1}
 \end{aligned}$$

Note: Once you get used to unit conversions, it may be easier to express the gas constant in units of $\text{dm}^3 \text{ bar mol}^{-1} \text{K}^{-1}$ (numerical value in these units is 0.083145). Other units can be used as long as they are consistent (*unit analysis is important!*). SI units are “automatically” compatible with each other.

The van der Waals equation fails in the neighborhood of the critical point:

$$|\bar{V}_c - \bar{V}| \propto (T_c - T)^{1/2} \quad (1.34)$$

However, experiments show that the exponent is close to 0.32 rather than 1/2. Other properties that depend on $(T_c - T)$ show similar discrepancies as well.

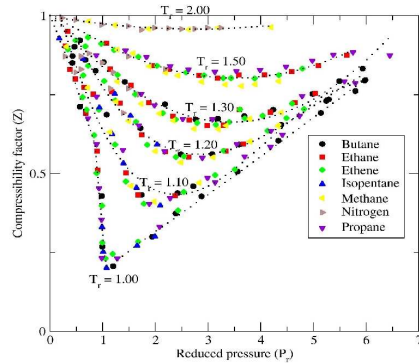
1.8 The principle of corresponding states

First we define reduced variables corresponding to P, T and \bar{V} as follows:

$$P_r = \frac{P}{P_c}, \bar{V}_r = \frac{\bar{V}}{\bar{V}_c}, T_r = \frac{T}{T_c} \quad (1.35)$$

By using these variables, it can be shown that the van der Waals equation becomes:

$$P_r = \frac{8T_r}{3\bar{V}_r - 1} - \frac{3}{\bar{V}_r^2} \quad (1.36)$$



Note that the gas dependent constants a and b disappeared from the equation. Thus within the van der Waals equation of state, all gases (regardless of their a and b values) should yield identical curves. The compressibility factor for van der Waals equation can also be expressed in reduced units:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r} \quad (1.37)$$

1.9 Description of the state of a system without chemical reactions

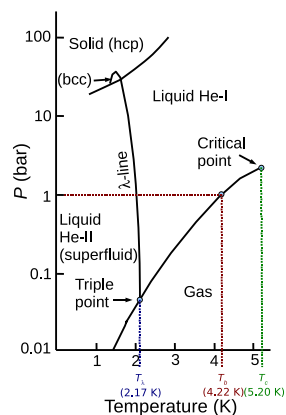
Intensive variables:

System	Degrees of freedom	Example choice of variables
One-phase	$F = 2$	$(T, P), (T, V), (P, V)$
Two-phase equilibrium	$F = 1$	T or P
Three-phase equilibrium	$F = 0$	none

Note: If multiple species (i.e., different gases) are included in one system then additional degrees of freedom must be specified (increases by $N_s - 1$, where N_s is the number of species; “the Gibbs phase rule”). Furthermore, a non-reactive system was assumed.

Extensive variables: one extensive variable per phase (i.e., the amount of each phase).

Example. Temperature of liquid ^4He ($T < 4$ K) can be determined from the helium vapor pressure in a closed container. Note that both liquid and gas phases coexist and thus only one variable is needed to specify the state of the system (both intensive variables). The experimentally observed phase diagram and the relation between helium vapor pressure and temperature are shown below.

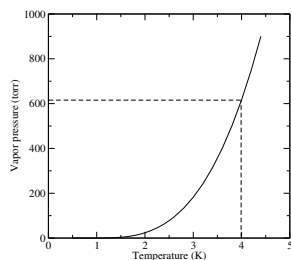


Helium phase diagram.

Example. For a non-reactive system with two species, two *extensive variables* are required for a complete description (i.e., the amount of each species).

Recall terminology: “intensive state of system” = “described by intensive variables” (i.e., they do not depend on the size of the system); “extensive state of system” = “described by extensive variables” (i.e., they depend on the size of the system).

Note: The choice of variables is not unique, only the number of variables is fixed.



The dashed line shows that 610 torr vapor pressure corresponds to 4 K.

1.10 Partial molar properties (gas mixtures)

A function is said to be homogenous of degree k if:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda^k f(x_1, x_2, \dots, x_N) \quad (1.38)$$

All *extensive variables* are homogeneous of degree $k = 1$:

$$V(\lambda n_1, \lambda n_2, \dots, \lambda n_N) = \lambda^1 V(n_1, n_2, \dots, n_N) = \lambda V(n_1, n_2, \dots, n_N) \quad (1.39)$$

where V is, for example, volume and n_i 's are amounts of gases.

All *intensive variables* are homogeneous of degree zero ($k = 0$):

$$T(\lambda n_1, \lambda n_2, \dots, \lambda n_N) = \lambda^0 T(n_1, n_2, \dots, n_N) = T(n_1, n_2, \dots, n_N) \quad (1.40)$$

Euler's theorem. If function f is homogeneous of degree k then the following holds:

$$kf(x_1, x_2, \dots, x_N) = \sum_{i=1}^N x_i \left(\frac{\partial f(x_1, x_2, \dots, x_N)}{\partial x_i} \right) \quad (1.41)$$

Proof. Function f is homogenous with degree k :

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_N) = \lambda^k f(x_1, x_2, \dots, x_N)$$

Differentiate both sides with respect to λ and apply the chain rule:

$$\sum_{i=1}^N \left\{ \frac{\partial f(\lambda x_1, \lambda x_2, \dots, \lambda x_N)}{\partial(\lambda x_i)} \times \underbrace{\frac{\partial(\lambda x_i)}{\partial \lambda}}_{=x_i} \right\} = k \lambda^{k-1} f(x_1, x_2, \dots, x_N)$$

This holds for all values of λ and therefore we can choose $\lambda = 1$:

$$\sum_{i=1}^N \frac{\partial f(x_1, x_2, \dots, x_N)}{\partial x_i} \times x_i = k f(x_1, x_2, \dots, x_N)$$

This completes the proof. If we apply this to volume V ($k = 1$), we have:

$$\begin{aligned} V &= \left(\frac{\partial V(n_1, n_2, \dots, n_N)}{\partial n_1} \right)_{T, P, \{n_j\}_{j \neq 1}} \times n_1 + \dots \\ &+ \left(\frac{\partial V(n_1, n_2, \dots, n_N)}{\partial n_N} \right)_{T, P, \{n_j\}_{j \neq N}} \times n_N = \bar{V}_1 n_1 + \bar{V}_2 n_2 + \dots + \bar{V}_N n_N \end{aligned} \quad (1.42)$$

where \bar{V}_i are referred to as partial molar volumes (m^3 / mol):

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} \quad (1.43)$$

Partial molar volume tells us in practice how much the volume changes when a small amount of gas component i is added to the gas mixture (P , T and the amounts of other components remain constant). In terms of differentials:

$$dV = \bar{V}_i dn_i \quad (1.44)$$

where dn_i is an infinitesimal change in the amount of component i and dV is the change in total volume occupied by the gas mixture. The total differential combining all the components is:

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 + \dots + \bar{V}_n dn_N \quad (1.45)$$

The non-differential form is convenient to write in terms of mole fractions (y_i):

$$\bar{V} = \bar{V}_1 y_1 + \bar{V}_2 y_2 + \dots + \bar{V}_N y_N \quad (1.46)$$

This result can be obtained by dividing both sides of Eq. (1.42) by n .

Example. Calculate the partial molar volume of a gas in an ideal gas mixture.

Solution. The volume of an ideal gas mixture is: $V = \frac{RT}{P} (n_1 + n_2 + \dots + n_N)$. The partial molar volumes can be calculated by using Eq. (1.43):

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} = \frac{RT}{P}$$

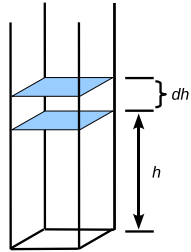
All of the gases in the mixture have identical partial molar volumes. This is not true for nonideal gases or liquids.

1.11 Barometric formula

In the following we calculate the effect of additional pressure arising from gravitation. This would be important, for example, if we consider a column of gas where a difference in gravitational force exists:

$$F = -mg \quad (1.47)$$

where m is the total mass of the gas and g is the standard gravitation constant (9.80665 m s^{-2}). To be exact, this constant depends on the position of measurement on earth. It can be as high as 10.7 m s^{-2} . In non-SI units the value of this constant is 32.2 ft s^{-2} .



Gas column with cross section area A .

The amount of gas within dh is:

$$dm_{gas} = \rho \times A \times dh \quad (1.48)$$

where ρ is the gas density (kg m^{-3}) and A is the column cross section. The force difference is given by:

$$dF = -dm_{gas}g = -\rho Agdh \quad (1.49)$$

Dividing both sides with A yields the pressure difference:

$$dP = \frac{dF}{A} = -\rho gdh \quad (1.50)$$

Note the sign convention in force ($-$ = down).

For an ideal gas, we have an expression for the gas density ρ :

$$PV = nRT \text{ and } \rho = \frac{nM}{V} \Rightarrow \rho = \frac{PM}{RT} \quad (1.51)$$

where M is the molar mass (kg mol^{-1}). Thus we have:

$$dP = -\frac{PM}{RT} gdh \quad (1.52)$$

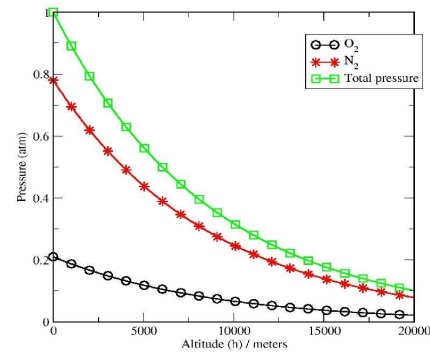
Separation of variables and integration from $h = 0$ (P_0) to h (P):

$$\int_{P_0}^P \frac{dP}{P} = - \int_0^h \frac{gM}{RT} dh \quad (1.53)$$

$$\ln \left(\frac{P}{P_0} \right) = -\frac{gMh}{RT} \quad (1.54)$$

$$P = P_0 e^{-\frac{gMh}{RT}} \quad (1.55)$$

This is known as *the barometric formula*.



Pressures of O₂ and N₂ and the total pressure of atmosphere at various heights as predicted by Eq. (1.55). It was assumed that the temperature does not depend on height (which is not quite true).

Chapter 2: First law of thermodynamics

“A system can exchange energy with its environment in the form of work or heat.”

2.1 Work and heat

Force (\vec{F}) acting on a particle is a vector quantity as it has a direction and magnitude. Newton's law of acceleration:

$$\vec{F} = m\vec{a} \quad (2.56)$$

where \vec{F} is the force (Newton, N), m the mass (kg) and \vec{a} the acceleration (m s^{-2}).

Work is a scalar quantity (in units of Joule):

$$w = \vec{F} \cdot \vec{L} = F_x L_x + F_y L_y + F_z L_z = |\vec{F}| |\vec{L}| \cos(\theta) \quad (2.57)$$

where \vec{L} is the vector defining the path (direction and length) along which the work is being done. Subscripts refer to the Cartesian components of the corresponding vectors.

Pressure P (Pa) is a scalar quantity:

$$P = \frac{F_{\perp}}{A} \quad (2.58)$$

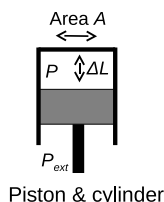
where F_{\perp} denotes the force component (N) that is perpendicular to the surface with area A (m^2).

Example. What is the work done on/by a moving piston inside a cylinder?

Solution. We assume *quasistatic* system: $P = P_{ext}$ at all times. This corresponds to slow movement of the piston.

The system consists of the piston and the cylinder and surroundings to outside of the cylinder. The work done on/by the the system (piston) is:

$$w = -F_{\perp} \Delta L = -P \underbrace{A \Delta L}_{\Delta V} = -P \Delta V$$



where the piston moved by ΔL and ΔV is the change in the cylinder volume. Note that ΔL and ΔV change sign depending on the process (i.e. compress or expand). Note the sign convention: “+” means that the surroundings did work on the system and “−” means that the system did work on the surroundings. The previous expressions can also be written using differentials. For example in this *quasistatic case* we have:

$$dw = -P_{ext} dV (= -PdV) \quad (2.59)$$

Example. What is the work done by a system *slowly* lifting an object weighting 1.00 kg by 0.100 m? The opposing force is the gravitational force.

Solution. The work is given by (note slow corresponds to a quasistatic system):

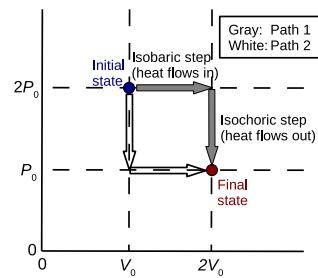
$$w = F \times h = -mgh = -(1.00 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (0.100 \text{ m}) = -0.981 \text{ J}$$

Integration of Eq. (2.59) yields an expression for work when $P = P(V, T)$:

$$w = - \int_{\text{point 1}}^{\text{point 2}} P_{\text{ext}}(V, T) dV \left(= - \int_{\text{point 1}}^{\text{point 2}} P(V, T) dV \right) \quad (2.60)$$

where the end points of the line integrals are located on the (P, V) plane.

Example. The state of a mole of gas can be changed from $(2P_0, V_0)$ to $(P_0, 2V_0)$ by infinitely many different quasistatic paths (two different choices are shown below):



Paths on the PV plane.

The total amount of work depends on the path!

Path 1:

1. Pressure is constant ($2P_0$), expansion from V_0 to $2V_0$ (heat flows in).
2. Volume is constant ($2V_0$), drop in pressure from $2P_0$ to P_0 (heat flows out). Total amount of work (w) = $-2P_0V_0$ (contribution from the first segment only).

Path 2:

1. Volume is constant (V_0), drop in pressure from $2P_0$ to P_0 (heat flows out).
2. Pressure is constant (P_0), expansion from V_0 to $2V_0$ (heat flows in). Total amount of work (w) = $-P_0V_0$ (contribution from the second segment only).

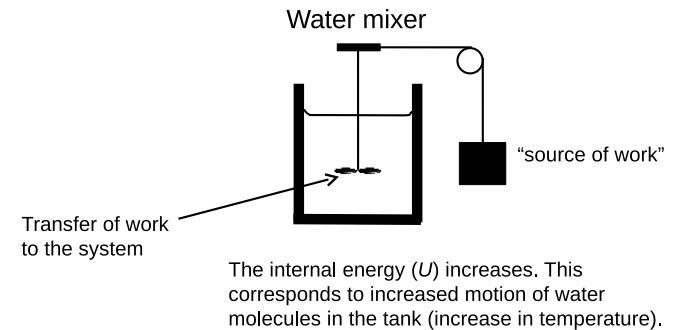
Adiabatic process: The system is thermally insulated and it cannot exchange heat with its surroundings. The two paths in the previous example involved heat exchange and therefore they were not adiabatic processes.

For an adiabatic process in a closed system, the change in system's internal energy (U) is directly related to work:

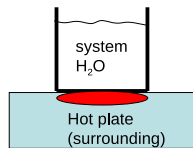
$$\Delta U = w \quad (2.61)$$

Note that ΔU follows the same sign convention that w does. Molar internal energy is expressed with a symbol \bar{U} (J mol^{-1}).

Example. A thermally insulated water tank with a stirrer.



Let's consider a water tank that is in thermal contact and has no stirrer (i.e. no source of work):



If the hot plate is warmer than the water, the water temperature increases (heat transfer). In previous example increase in system temperature was achieved by doing work on the system. Thus increase in the internal energy of the system can be achieved either by *doing work on it* or by *transferring heat into it*.

Both work and heat are forms of energy crossing the boundary between the system and the surroundings. When no work is done on the system, the change in its internal energy can be expressed as:

$$\Delta U = q \text{ (no work done)} \quad (2.62)$$

Both work and heat have the same SI unit (J).

2.2 First law of thermodynamics and internal energy

The first law of thermodynamics states that:

$$\Delta U = q + w \quad (2.63)$$

$$dU = dq + dw \quad (2.64)$$

Note that q and w indicate changes in heat and work – in this sense Δ is “missing” in this notation.

The above equations are obtained by combining the results from previous section for work and heat. The internal energy of a system (U) is a function of state variables (for example, P, V, T ; closed system). Internal U energy is an extensive property.

The differential corresponding to the internal energy, dU , yields zero when integrated over a closed loop in the state space:

$$\oint dU = 0 \quad (2.65)$$

However, the component differentials dq and dw do not have this property.

Energy may be transferred in one form or another, but it cannot be created or destroyed (energy conservation).

U depends on state variables, e.g. $U(T, V, n)$ or $U(T, P, n)$ for pure substances. For mixtures, the composition must also be specified.

2.3 Exact and inexact differentials

A differential with two independent degrees of freedom, can be expressed as (“Pfaffian form”):

$$du = M(x, y)dx + N(x, y)dy \quad (2.66)$$

For *exact differential* du functions M and N must correspond to some derivatives of u . However, in general, there are differentials for which this does not hold. Such differentials are called *inexact differentials*.

Test for exact differentials. Differential du is exact if and only if:

$$\left(\frac{\partial N(x, y)}{\partial x} \right)_y = \left(\frac{\partial M(x, y)}{\partial y} \right)_x \quad (2.67)$$

Example. Show that the following differential is exact:

$$du = \underbrace{\left(2xy + \frac{9x^2}{y} \right)}_{=M} dx + \underbrace{\left(x^2 - \frac{3x^3}{y^2} \right)}_{=N} dy$$

Solution. To show this, we verify that Eq. (2.67) holds:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left[\frac{\partial}{\partial y} \left(2xy + \frac{9x^2}{y} \right) \right]_x = 2x - \frac{9x^2}{y^2}$$

$$\left(\frac{\partial N}{\partial x} \right)_y = \left[\frac{\partial}{\partial x} \left(x^2 - \frac{3x^3}{y^2} \right) \right]_y = 2x - \frac{9x^2}{y^2}$$

Because both partial derivatives are equal, differential du is exact.

For functions with three independent variables, the Pfaffian form is:

$$du = M(x, y, z)dx + N(x, y, z)dy + P(x, y, z)dz \quad (2.68)$$

and the corresponding condition for exactness is now:

$$\begin{aligned} \left(\frac{\partial M}{\partial y} \right)_{x,z} &= \left(\frac{\partial N}{\partial x} \right)_{y,z} \\ \left(\frac{\partial N}{\partial z} \right)_{x,y} &= \left(\frac{\partial P}{\partial y} \right)_{x,z} \\ \left(\frac{\partial M}{\partial z} \right)_{x,y} &= \left(\frac{\partial P}{\partial x} \right)_{y,z} \end{aligned} \quad (2.69)$$

Example. Show that the following differential is not exact but it can be transformed into an exact differential by dividing both sides by x .

$$du = \underbrace{(2ax^2 + bxy)}_{=M} dx + \underbrace{(bx^2 + 2cxy)}_{=N} dy$$

Solution. Calculate the required partial derivatives and use Eq. (2.67):

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y} (2ax^2 + bxy)\right]_x = bx$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \left[\frac{\partial}{\partial x} (bx^2 + 2cxy)\right]_y = 2bx + 2cy \neq bx$$

Thus the original differential is not exact. After dividing du by x , however:

$$\left(\frac{\partial M'}{\partial y}\right)_x = \left[\frac{\partial}{\partial y} (2ax + by)\right]_x = b$$

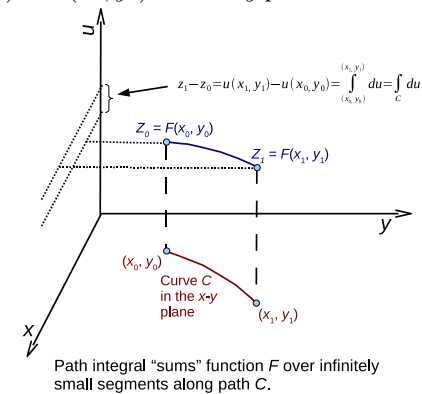
$$\left(\frac{\partial N'}{\partial x}\right)_y = \left[\frac{\partial}{\partial x} (bx + 2cy)\right]_y = b$$

This procedure of transforming an inexact differential into an exact one is called the *method of integrating factors*.

Line integrals are evaluated over a specified path in the x - y (or in higher dimensional spaces):

$$\int_{(x_0, y_0)}^{(x_1, y_1)} du = \int_{(x_0, y_0)}^{(x_1, y_1)} [M(x, y)dx + N(x, y)dy] \quad (2.70)$$

However, this is not yet well defined because there are infinitely many paths that connect points (x_0, y_0) and (x_1, y_1) in the x - y plane. One such path is shown below:



An integration path (C) must be specified for line integrals:

$$\int_C du = \int_C [M(x, y)dx + N(x, y)dy] \quad (2.71)$$

Note that line integrals are sometimes also called path integrals.

When the integration path is defined by functions $y = y(x)$ and $x = x(y)$, the line integral along this path can be calculated as:

$$\int_C du = \int_{x_0}^{x_1} M(x, y(x))dx + \int_{y_0}^{y_1} N(x(y), y)dy \quad (2.72)$$

Example. Find the value of the following line integral:

$$\int_C du = \int_C [(2x + 3y)dx + (3x + 4y)dy]$$

where path C is the straight-line segment given by $y = 2x + 3$ from $(0, 3)$ to $(2, 7)$.

Solution. In the first term, y must be replaced by $2x + 3$, and in the second term x must be replaced by $(1/2)(y - 3)$,

$$\begin{aligned} \int_C du &= \int_0^2 [2x + 3(2x + 3)] dx + \int_3^7 \left[\frac{3}{2}(y - 3) + 4y \right] dy \\ &= \left(\frac{8x^2}{2} + 9x \right) \Big|_0^2 + \left(\frac{11y^2/2}{2} - \frac{9}{2}y \right) \Big|_3^7 = 126 \end{aligned}$$

If differential du is exact, then *the line integral does not depend on path* but only on the end points:

$$\int_C du = \int_C \left[\left(\frac{\partial u}{\partial x} \right) dx + \left(\frac{\partial u}{\partial y} \right) dy \right] = u(x_1, y_1) - u(x_0, y_0) \quad (2.73)$$

For closed paths, this always yields zero (*this does not hold for inexact differentials*):

$$\oint du = 0 \text{ (over a closed loop)} \quad (2.74)$$

Example. Show that the line integral of the previous example has the same value as the line integral of the same differential on the rectangular path from $(0, 3)$ to $(2, 3)$ and then to $(2, 7)$.

Solution. The integration path is not a single curve but two line segments. So we must carry out the integration separately for each segment. On the first segment, y is constant, so $dy = 0$ and the integral containing dy vanishes. On the second line segment, x is constant, so $dx = 0$ and the integral containing dx vanishes:

$$\int_C du = \int_0^2 (2x + 9)dx + \int_3^7 (6 + 4y)dy = \left(\frac{2x^2}{2} + 9x \right) \Big|_0^2 + \left(6y + \frac{4y^2}{2} \right) \Big|_3^7 = 126$$

Note that this is the same result as obtained in the previous example.

Example. Show that differential $du = dx + xdy$ is inexact and carry out line integration using two different paths between points $(0,0)$ and $(2,2)$. Path 1 is defined as: straight line from $(0,0)$ to $(2,2)$ and path 2 as: rectangular path $(0,0)$ to $(2,0)$ to $(2,2)$.

Solution. First we show that the differential is inexact:

$$\left[\frac{\partial}{\partial y}(1) \right]_x = 0 \text{ and } \left[\frac{\partial}{\partial x}(x) \right]_y = 1 \neq 0$$

$$\Rightarrow du \text{ is inexact differential.}$$

Integration along path 1 (denoted by C_1 , a straight line $y = x$):

$$\int_{C_1} du = \int_{C_1} dx + \int_{C_1} xdy = \int_0^2 dx + \int_0^2 ydy = x|_0^2 + \frac{y^2}{2} \Big|_0^2 = 4$$

Integration along path 2 (denoted by C_2):

$$\int_{C_2} du = \int_{C_2} dx + \int_{C_2} xdy = \int_0^2 dx + \int_0^2 2dy = x|_0^2 + 2y|_0^2 = 2 + 4 = 6$$

Thus the value of the line integral depends on path. This is because du is inexact.

For three independent variables, line integral is defined as:

$$\int_C du = \int_C [M(x, y, z)dx + N(x, y, z)dy + P(x, y, z)dz] \quad (2.75)$$

Furthermore, the integral can be evaluated using:

$$\int_C du = \int_{x_0}^{x_1} M(x, y(x), z(x))dx + \int_{y_0}^{y_1} N(x(y), y, z(y))dy + \int_{z_0}^{z_1} P(x(z), y(z), z)dz \quad (2.76)$$

If du is exact differential, the value of the line integral depends *only* on the endpoints:

$$\int_C du = u(x_1, y_1, z_1) - u(x_0, y_0, z_0) \quad (2.77)$$

In general, for cyclic processes:

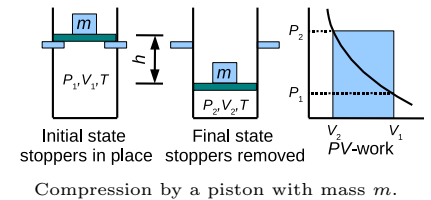
$$\oint du = 0 \quad (\text{only if } du \text{ is exact}) \quad (2.78)$$

2.4 Work of compression and expansion of a gas at constant temperature

Work can be done on/by a gas upon compression/expansion. In the following example gas is the system and the surroundings constitutes of a piston and a thermostat (i.e. a container that keeps the temperature constant).

Assumptions:

- ▶ No friction
- ▶ No external pressure outside the cylinder (from atmosphere)
- ▶ Cylinder immersed in a thermostat (constant T)



Consider a two stage process:

1. Pressure P_1 , Volume V_1 and Temperature T (stoppers removed but the piston has not yet fallen down due to gravity).
2. Pressure P_2 , Volume V_2 and Temperature T (the piston has fallen down).

At both points the external pressure is $P_{ext} = \frac{mg}{A}$ where A is the area of the piston. Thus the force pushing the piston down is mg . At the end of the process the gas pressure will be the same as the external pressure: $P_{ext} = P_2$. Recall that work was defined as “force \times distance”, which in this case means (see Eq. (2.60), $P_1 < P_2$):

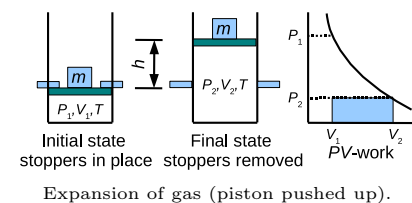
$$w_{comp} = \int_{ini}^{fin} dw = \int_{ini}^{fin} \underbrace{-P_{ext}}_{\text{constant}} dV = -P_2(V_2 - V_1) = P_2(V_1 - V_2) > 0 \quad (2.79)$$

or expressed in another way without reference to P_2 :

$$w_{comp} = \int_{ini}^{fin} \underbrace{-P_{ext}}_{\text{constant}} dV = \frac{mg}{A} \times \underbrace{(Ah)}_{=\Delta V} = mg \times h \text{ (force} \times \text{distance)} \quad (2.80)$$

where the positive sign for w_{comp} signifies that work was done on the system and h denotes the distance that the piston moved (the shaded area on the previous page P - V plot).

Next, consider expansion of a gas in a two stage process:



Work done by the system is given by ($P_1 > P_2$, $P_2 = P_{ext}$):

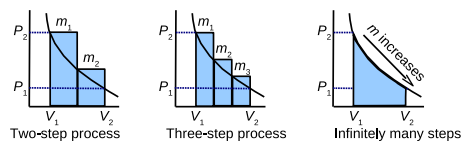
$$w_{exp} = \int_{ini}^{fin} \underbrace{-P_{ext}}_{\text{constant}} dV = -P_{ext}(V_2 - V_1) = P_2(V_1 - V_2) < 0 \quad (2.81)$$

Note: $|w_{comp}| > |w_{exp}|$. More work is required to compress the gas than can be obtained by expansion. This process is **irreversible**.

Is it possible to move the piston in such a way that $|w_{exp}| = |w_{comp}|$? In other words, is it possible to make the process **reversible** in terms of work?

59

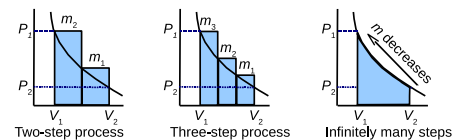
Yes. Instead of single-step compression, we should use many compression steps with increasing external pressure P_{ext} . This can be achieved by increasing the mass gradually ($m_1 < m_2 < m_3 < \dots$):



In other words: do not apply all the force at once but increase it gradually. *Note that in a reversible process the pressure inside the cylinder and the external pressure are equal at all times.* In this case the work is obtained by (P is the pressure inside the cylinder):

$$w_{comp} = \int_{ini}^{fin} d\mathbf{w} = - \int_{V_1}^{V_2} P_{ext} dV = - \int_{V_1}^{V_2} P dV \quad (2.82)$$

Expansion work w_{exp} can also be carried out using infinite expansion steps ($m_1 > m_2 > m_3 \dots$):



This infinite expansion process is also reversible. The expression for work is now:

$$w_{exp} = \int_{ini}^{fin} d\mathbf{w} = - \int_{V_2}^{V_1} P dV \quad (2.83)$$

Work over one closed cycle (reversible compression followed by reversible expansion):

$$w_{cycle} = \underbrace{- \int_{V_1}^{V_2} P dV}_{\text{compression}} - \underbrace{\int_{V_2}^{V_1} P dV}_{\text{expansion}} = - \int_{V_1}^{V_2} P dV + \int_{V_1}^{V_2} P dV = 0 \quad (2.84)$$

Thus the infinitesimal process is reversible. Many calculations can be carried out exactly only for reversible processes. Most processes in nature are, however, irreversible. Sometimes they can be approximated as reversible processes.

For a reversible process $P_{ext} = P$ (in the cylinder) always. Assuming that the gas in the cylinder is ideal, we have for *reversible expansion* (T constant, $V_1 < V_2$, $ini = 1$ and $fin = 2$):

$$w_{exp,rev} = - \int_{V_1}^{V_2} P_{ext} dV = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \left(\frac{V_2}{V_1} \right) \quad (2.85)$$

For reversible compression (T constant, $V_1 > V_2$, $ini = 1$ and $fin = 2$), we have $w_{comp,rev} = -nRT \ln \left(\frac{V_2}{V_1} \right) > 0$.

For an ideal gas at constant temperature, we have $P_1 V_1 = P_2 V_2$ and Eq. (2.85) can then be written:

$$w_{exp,rev} = -nRT \ln \left(\frac{V_2}{V_1} \right) = -nRT \ln \left(\frac{P_1}{P_2} \right) = nRT \ln \left(\frac{P_2}{P_1} \right) \quad (2.86)$$

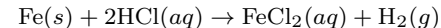
The maximum amount of work of isothermal expansion of a van der Waals gas is:

$$w_{exp,rev} = - \int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2} \right) dV = -nRT \ln \left(\frac{V_2-nb}{V_1-nb} \right) + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \quad (2.87)$$

Note: During reversible processes the system and the surroundings are in equilibrium. However, such processes are ideal since they take infinitely long time to proceed.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺ ↻

Example. Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25 °C (reversible). The reaction is:



Assume that H_2 follows the ideal gas law.

Solution.

- (a) The volume cannot change, so no PV -work is done and $w_{exp} = 0$.
 (b) The gas drives back the atmosphere and therefore $w_{exp} = -P_{ext} \Delta V$. We can neglect the initial volume (V_1) because the final volume (V_2) after production of gas, is much larger. We assume that H_2 behaves according to the ideal gas law (n moles of H_2):

$$\Delta V = V_2 - V_1 \approx V_2 = \frac{nRT}{P} = \frac{nRT}{P_{ext}}$$

where P is the gas pressure and P_{ext} the atmospheric pressure. Note that solids have negligible volumes compared to gases and therefore we have:

$$w_{exp} = -P_{ext} \Delta V \approx -P_{ext} \times \frac{nRT}{P_{ext}} = -nRT$$

When 1 mol of Fe is consumed in the reaction, 1 mol H_2 is produced.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺ ↻

Because the molar mass of Fe is 55.85 g mol⁻¹, it follows that:

$$w_{exp} \approx -\frac{50 \text{ g}}{55.85 \text{ g mol}^{-1}} \times (8.3145 \text{ JK}^{-1}\text{mol}^{-1}) \times (298.15 \text{ K}) = -2.2 \text{ kJ}$$

Thus the system (H₂ gas from the reaction) does 2.2 kJ of work driving back the atmosphere.

Example. Work of expansion of an ideal gas. One mole of an ideal gas expands from 5 to 1 bar at 298 K. Calculate w_{exp} (a) for reversible expansion and (b) for an irreversible expansion against a constant external pressure of 1 bar.

Solution. (a) We use Eq. (2.86) with $P_1 = 5 \text{ bar}$ (*ini*) and $P_2 = 1 \text{ bar}$ (*fin*):

$$w_{exp,rev} = nRT \ln \left(\frac{P_2}{P_1} \right) = (1 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{1 \text{ bar}}{5 \text{ bar}} \right)$$

(b) The irreversible work $w_{exp,irrev}$ is given by Eq. (2.81):

$$w_{exp,irrev} = -P_2 (V_2 - V_1) = -P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = nRT \left(\frac{P_2}{P_1} - 1 \right)$$

$$(1 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \left(\frac{1 \text{ bar}}{5 \text{ bar}} - 1 \right) = -2000 \text{ J}$$

2.5 Various kinds of work

The following are most often encountered types of work:

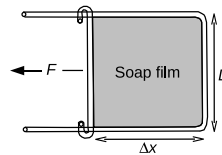
Type of work	Differential	Comments	Conjugate pairs
Expansion, Hydrostatic	$-P_{ext}dV$	“ PV -work”	Pressure P , Volume V
Surface expansion	γdA_s	γ is surface tension and A_s is surface area	γ and A_s
Extension, elongation	FdL	Change in length	Force F , Length l
Electrical	ϕdQ	Transport of electrons	Potential difference ϕ , Electric charge Q

Surface tension (γ): “Force / distance” (unit N m^{-1}):

$$\gamma = \frac{F}{L} \quad (2.88)$$



Surface tension of water.



Idealized experiment to determine surface tension.

For a film with two sides, the force F acting on the bar (L is the width) is given by:

$$F = 2\gamma L \quad (2.89)$$

Work corresponding to moving the bar by Δx is given by (“force \times distance”):

$$w = F\Delta x \quad (2.90)$$

By combining these two equations we get:

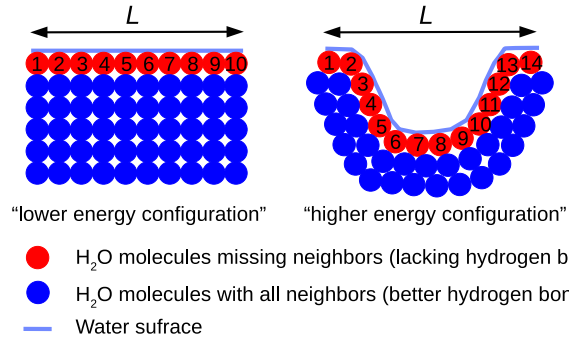
$$w = F\Delta x = \gamma \underbrace{2L\Delta x}_{=\Delta A_s} = \gamma \Delta A_s \quad (2.91)$$

The differential form of Eq. (2.91) is:

$$dw = \gamma dA_s \quad (2.92)$$

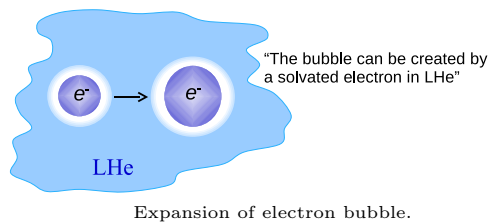
In other words, to get work w , multiply the surface area (m^2) by surface tension (J m^{-2}). Note that units N m^{-1} and J m^{-2} are equivalent.

What is the microscopic origin of surface tension? Consider water surface, for example:



Molecules residing on the curved surface are missing neighboring atoms which they could hydrogen bond with. Surface tension depends clearly on the molecule – molecule (or atom – atom) interaction strength. For example, surface tension of water (hydrogen bonding) is much larger than for liquid argon (van der Waals binding).

Example. Calculate the amount of work that a spherical bubble in superfluid ^4He does when its radius changes from 10 \AA to 20 \AA . Surface tension of L-He γ is $0.18 \text{ cm}^{-1} \text{ \AA}^{-2}$.



The differential surface area of the bubble is given by:

$$dA_s = 4\pi(r + dr)^2 = \underbrace{4\pi r^2}_{\text{constant}} + 8\pi r dr + \underbrace{4\pi(dr)^2}_{\text{2nd order}} \rightarrow 8\pi r dr$$

Eq. (2.92) now gives: $d\mathcal{W} = \gamma dA_s = 8\pi r \gamma dr$

Integration from the initial radius r_i to the final radius r_f gives:

$$w = \int_{r_i}^{r_f} d\mathcal{W} = 8\pi\gamma \int_{r_i}^{r_f} r dr = 4\pi\gamma (r_f^2 - r_i^2)$$

We could proceed by changing everything to SI units, but here the expression is quite simple and we just make sure to use compatible units:

$$w = 4\pi \times (0.18 \text{ cm}^{-1} \text{ \AA}^{-2}) \times [(20 \text{ \AA})^2 - (10 \text{ \AA})^2] = 680 \text{ cm}^{-1} = 1.4 \times 10^{-20} \text{ J}$$

Surface tension work can also be understood in terms of surface energy.

Notes:

- ▶ The work in above example is positive, which means that work was done on the bubble interface (i.e., interface area becomes larger).
- ▶ Recall that we don't usually use notation Δw to indicate change in work because work is a relative quantity. The same applies for q . Instead of Δw , we just use w .

Extension/elongation work:

$$d\mathcal{W} = F dL \quad (2.93)$$

where F is the extension force and dL is the displacement. For example: elongation of a rubber band.

2.6 Change in state at constant volume

Previously we have kept temperature constant and concentrated on the concept of work. In this section, under constant volume, heat must also be considered (here work w will be zero). The amount of heat (q) can be measured by determining the change in temperature of a mass of material that absorbs the heat. The heat capacity (C) of the system is defined as:

$$C = \frac{dq}{dT} \text{ or } CdT = dq \quad (2.96)$$

where the heat capacity acts as a proportionality constant between change in temperature and the amount of heat. Notice that the differential corresponding to heat is *inexact*. This means that a path must be specified along which the differential is evaluated.

For a chemically inert system we can use two variables for describing the system (T and V chosen here). Because the internal energy U is a state function (i.e. the corresponding differential is exact), we have the total differential of U :

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (2.97)$$

Substituting $dU = dq - P_{ext}dV$ in Eq. (2.97) gives (only PV -work included):

$$dq = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV \quad (2.98)$$

By choosing the path in such a way that the volume V is constant, we have $dV = 0$ and:

69

Electrical work:

$$dw = \phi dQ \quad (2.94)$$

where ϕ is the electric potential difference and dQ is the differential change in charge. For example: electron transport in electrolytic cell.

A more complete form of the first law is ("heat dq + work dw "):

$$dU = dq - P_{ext}dV + \gamma dA_s + FdL + \phi dQ \quad (2.95)$$

$$dq_V = \left(\frac{\partial U}{\partial T} \right)_V dT \quad (2.99)$$

Both the temperature and the heat transfer can be measured and thus it is convenient to define heat capacity $C_V(T)$ at constant volume as:

$$C_V(T) \equiv \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T} \right)_V \quad (2.100)$$

For one mole of substance, heat capacity is denoted by \bar{C}_V .

Note: Temperature and heat are two different quantities. On molecular scales temperature is related to the kinetic energy distribution of molecules in the substance. Heat is related to the total energy of molecules (including potential energy).

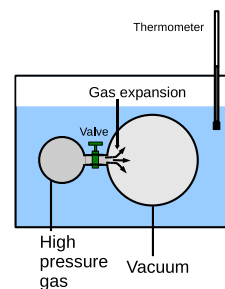
At constant volume, Eq. (2.100) may be multiplied by dT and integrated (see also Eq. (2.99)):

$$\Delta U_V = \int_{T_1}^{T_2} C_V(T) dT = q_V \quad (2.101)$$

If C_V is approximately constant between T_1 and T_2 , we can simplify the above result:

$$\Delta U_V \approx C_V (T_2 - T_1) = C_V \Delta T \quad (2.102)$$

Now we know what $\left(\frac{\partial U}{\partial T} \right)_V$ means but how about $\left(\frac{\partial U}{\partial V} \right)_T$? To see this, we keep T constant (Eq. (2.97)):



Joule's experiment: Gas expands into vacuum

$$dq = \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV \quad (2.103)$$

Joule found in his experiments that $\Delta T \approx 0$ and therefore $q \approx 0$. Rigorously this can be shown to hold for ideal gases. This implies that for ideal gases we have:

$$dq = 0 \quad (2.104)$$

If we consider an ideal gas in a process where $P_{ext} = 0$ and $dV \neq 0$ (Joule's experiment), it follows that (Eq. (2.103)):

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \text{ for an ideal gas} \quad (2.105)$$

This result does not hold for real gases. In real gases molecules interact with each other and a change in volume affects the average distance between molecules.

2.7 Enthalpy and change of state at constant pressure ⁷³

Constant-pressure processes are more common in chemistry than constant-volume processes because many experiments are carried out in open vessels. If only pressure-volume work is done and the pressure is constant and equal to the applied pressure (P_{ext}), we have $w_P = -P_{ext}\Delta V = -P\Delta V$ (P is the pressure of the system; quasi-static system). Now the change in internal energy (ΔU) can be written as (see Eq. (2.63)):

$$\Delta U = q_P + w_P = q_P - P\Delta V \quad (2.106)$$

where subscript P refers to a process at constant pressure (i.e. isobaric process).

Denote the initial state by 1 and the final state by 2 and write ΔU and ΔV explicitly:

$$U_2 - U_1 = q_P - P(V_2 - V_1) \quad (2.107)$$

Rearranging terms gives:

$$q_P = \underbrace{(U_2 + PV_2)}_{=H_2} - \underbrace{(U_1 + PV_1)}_{=H_1} = H_2 - H_1 = \Delta H \quad (2.108)$$

where we have used notation $H = U + PV$ and H is the *enthalpy*.

From Eq.(2.108) it also follows that the differentials corresponding to heat (dq_P) and enthalpy (dH) must be equal (at constant pressure):

$$dq_P = dH \quad (H \text{ is a state function and } dH \text{ is exact}) \quad (2.109)$$

Because dH is an exact differential, we can write the total differential as:

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad (2.110)$$

Under constant pressure $dP = 0$ and if we combine Eqs. (2.109) and (2.110), we get:

$$dq_P = \left(\frac{\partial H}{\partial T} \right)_P dT \quad (2.111)$$

We can now define heat capacity at constant pressure (C_P) as follows:

$$C_P \equiv \frac{dq_P}{dT} = \left(\frac{\partial H}{\partial T} \right)_P \quad (2.112)$$

Integration of Eq. (2.111) gives an expression for change in enthalpy (cf. Eq. (2.102)):

$$\Delta H_P = \int_{T_1}^{T_2} C_P(T) dT \approx C_P \Delta T \quad (\text{if } C_P \text{ constant over } T_1, T_2) \quad (2.113)$$

Example. Enthalpy change can be measured with a constant-pressure calorimeter. A simple example of such calorimeter is the “coffee-cup-calorimeter”. 10.0 g of ice at 273 K is added to such calorimeter containing 100.0 g of water at 303 K. The heat capacity of the calorimeter is 10.0 J K⁻¹. What is the final temperature of the water in the cup? It was observed that all ice melted and therefore we know that all ice was transformed to water.



Solution. Overall, the enthalpy is conserved (thermal insulation):

$$\underbrace{\Delta H_{\text{ice melts}} + \Delta H_{\text{cold water warms to final temp.}}}_{\text{added ice}} + \underbrace{\Delta H_{\text{water cools}}}_{\text{water present in the cup}} + \underbrace{\Delta H_{\text{apparatus cools}}}_{\text{coffee cup}} = 0$$

Enthalpy change for the melting process can be obtained by multiplying the mass of ice by the enthalpy of fusion (will be discussed in more detail later):

$$\Delta H_{\text{ice melts}} = m_{\text{ice}} \Delta_{\text{fus}} H = (10.0 \text{ g}) \times \underbrace{(333 \text{ J g}^{-1})}_{\text{from table}} = 3330 \text{ J}$$

Next we calculate the change in enthalpy when water at 273 K warms up to the final temperature (see Eq. (2.113)):

where T_f denotes the (still unknown) final temperature. On the other hand, the water initially at 303 K cools down to the final temperature T_f :

$$\underbrace{\Delta H_{\text{water cools}}}_{\text{cools}} = m_{\text{water}} C_{P, \text{H}_2\text{O}} \Delta T = (100.0 \text{ g}) \times (4.19 \text{ J g}^{-1} \text{ K}^{-1}) \times (T_f - 303 \text{ K})$$

Finally, we have to consider cooling of the calorimeter from 303 K down to the final temperature:

$$\underbrace{\Delta H_{\text{apparatus cools}}}_{\text{cools}} = C_{\text{calorimeter}} \Delta T = (10.0 \text{ J K}^{-1}) \times (T_f - 303 \text{ K})$$

Because the net change in enthalpy is zero (conservation of enthalpy), we can solve for T_f :

$$(3330 \text{ J}) + (41.9 \text{ J K}^{-1}) \times (T_f - 273 \text{ K}) + (419 \text{ J K}^{-1}) \times (T_f - 303 \text{ K}) \\ + (10.0 \text{ J K}^{-1}) \times (T_f - 303 \text{ K}) = 0 \Rightarrow T_f = 293 \text{ K}$$

Note: In non-SI units the temperatures correspond to:

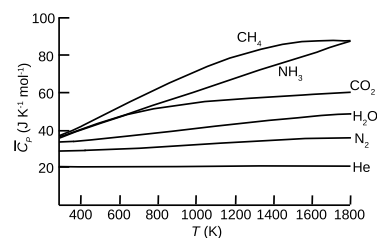
273 K = 31.7 °F = 0 °C (ice)

293 K = 67.6 °F = 20 °C (final temperature)

303 K = 85.7 °F = 30 °C (water)

2.8 Heat capacities

Values for molar heat capacities can be found, for example, from the National Institute of Standards and Technology (NIST) database (<http://webbook.nist.gov/chemistry/>). It has been observed experimentally that molar heat capacities at constant pressure depend on temperature.



Empirical power series expansion:

$$\bar{C}_P \approx \alpha + \beta T + \gamma T^2 \quad (2.114)$$

Inserting this form into Eq. (2.113) gives:

$$\Delta H = \alpha (T_2 - T_1) + \frac{\beta}{2} (T_2^2 - T_1^2) + \frac{\gamma}{3} (T_2^3 - T_1^3) \quad (2.115)$$

Values for α , β and γ are given in the above database. Note that the temperature range for these polynomial fits must be observed. In above, 1 refers to the initial and 2 to the final state

The relation between C_P and C_V :

Consider Eq. (2.98) at constant volume and pressure (with pressure $P = P_{ext}$):

$$dq_P = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV = C_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV \quad (2.116)$$

$$\text{division by } dT \Rightarrow \underbrace{\frac{dq_P}{dT}}_{=C_P} = C_V + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow C_P - C_V = \left[P_{ext} + \underbrace{\left(\frac{\partial U}{\partial V} \right)_T}_{(\text{term 1})} \right] \times \underbrace{\left(\frac{\partial V}{\partial T} \right)_P}_{(\text{term 2})} > 0$$

where “term 1” is greater than zero (consider, for example, a van der Waals gas where this term is equal to a/\bar{V}) and “term 2” is also greater than zero because, at constant pressure, increase in temperature will result in increased volume. Thus we conclude that heat capacity at constant pressure is always greater than the heat capacity at constant volume. This is not surprising because the former also includes the PV -work and the work required to pull molecules apart.

Example. Calculate $C_P - C_V$ for an ideal gas (reversible process). Note that in ideal gas, the gas molecules do not interact with each other.

Solution. To calculate the difference in heat capacities, we use Eq. (2.116). Because molecules do not interact with each other, the internal energy does not depend on volume. Hence $(\partial U / \partial V)_T = 0$. For an ideal gas, we have $PV = nRT$, from which we can evaluate the partial derivative $(\partial V / \partial T)_P = nR/P$. Inserting the partial derivatives into Eq. (2.116) gives $C_P - C_V = nR$. This is the PV -work required when temperature changes by 1 K.

Notes:

- Classical thermodynamics does not deal with molecular level information. It knows nothing about atoms and molecules. In fact, when classical thermodynamics was first developed, scientists did not know about atoms and molecules at all.
- For liquids and solids, $C_P \approx C_V$ because they have small thermal expansivities.

Results from the kinetic gas theory results for monoatomic ideal gas:

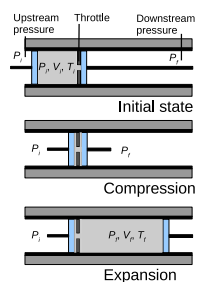
$$\bar{U} = \frac{3}{2}RT \quad (2.117)$$

$$\bar{H} = \frac{5}{2}RT \quad (2.118)$$

$$\bar{C}_V = \frac{3}{2}R \quad (2.119)$$

$$\bar{C}_P = \frac{5}{2}R \quad (2.120)$$

2.9 Joule-Thomson expansion



Joule and Thomson (aka Lord Kelvin) observed a change in gas temperature when it was expanded through a throttle. To push one mole of gas through the throttle, two processes must be considered (temperatures remain constants on each side; they might, however, be different):

1. Compression of gas on the left
2. Expansion of gas on the right

On *compression*, the work is given by $w_c = P_i \Delta \bar{V} = P_i (\bar{V}_i - \bar{V}_f) = P_i (\bar{V}_i - 0) = P_i \bar{V}_i$ (positive because work is done on the system (gas)).

On *expansion*, the work is now $w_e = P_f \Delta \bar{V} = P_f (\bar{V}_i - \bar{V}_f) = P_f (0 - \bar{V}_f) = -P_f \bar{V}_f$ (negative because work is done by the system (gas)).

The total amount of work (for the gas) is then:

$$w = w_c + w_e = P_i \bar{V}_i - P_f \bar{V}_f \quad (2.121)$$

81



James Prescott Joule, English physicist (1818 - 1889)

The system is thermally insulated, so that $q = 0$ (no heat exchange). Using Eq. (2.63) we obtain:

$$\Delta \bar{U} = \bar{U}_f - \bar{U}_i = q + w = P_i \bar{V}_i - P_f \bar{V}_f \quad (2.122)$$

Rearrangement of this equation gives:

$$\underbrace{\bar{U}_f + P_f \bar{V}_f}_{=H_f} = \underbrace{\bar{U}_i + P_i \bar{V}_i}_{=H_i} \quad (2.123)$$

This states that the enthalpy is conserved in the process (*isenthalpic process*). Based on the experimental observation, we define the Joule-Thomson coefficient:

$$\mu_{JT} = \lim_{\Delta P \rightarrow 0} \frac{T_2 - T_1}{P_2 - P_1} = \left(\frac{\partial T}{\partial P} \right)_H \quad (2.124)$$

which gives the change in temperature when pressure changes. At high temperatures the coefficient is negative (J-T process results in heating) and at low temperatures it is positive (J-T process results in cooling). The temperature, where the coefficient is zero, is called the *inversion temperature*. The inversion temperature for N_2 is 607 K and for H_2 204 K.

Notes:

- ▶ The J-T coefficient is zero for ideal gases: $0 = \left(\frac{\partial H}{\partial P} \right)_H = \frac{5}{2} nR \left(\frac{\partial T}{\partial P} \right)_H$.
- ▶ The cooling effect can be understood by decrease in the van der Waals interaction due to lower pressure (i.e. increased potential energy) and decrease in the kinetic energy (i.e. lower temperature).

2.10 Adiabatic processes with gases

In an adiabatic process no heat is exchanged with the surroundings ($dq = 0$). If only PV -work is involved, then the first law (Eq. (2.64)) states that:

$$dU = dq + dw = dw = -P_{ext}dV \quad (2.125)$$

If work is done against external pressure, the temperature of the system drops (note: adiabatic process; no thermal contact). If the system was in thermal contact, the system would exchange heat with its surroundings and the temperature would remain constant.

Consider an ideal gas. The change in internal energy (ΔU) depends only on temperature and not on volume (Eqs. (2.97), (2.105), (2.100)):

$$dU = C_V dT, \text{ if } C_V \text{ is independent of } T, \text{ we have: } \Delta U = C_V \Delta T \quad (2.126)$$

On the other hand, we know that $\Delta U = w$ and therefore $w = C_V \Delta T$. Furthermore, we know that $w = -P_{ext} \Delta V$, which means that $-P_{ext} \Delta V = C_V \Delta T$. This predicts that upon increase in volume, the temperature decreases, for example.

When adiabatic expansion is carried out reversibly, the equilibrium pressure can be substituted for the external pressure ($P_{ext} = P$). For an ideal gas we have:

$$\bar{C}_V dT = -Pd\bar{V} = -\frac{RT}{\bar{V}} d\bar{V} \Rightarrow \bar{C}_V \frac{dT}{T} = -R \frac{d\bar{V}}{\bar{V}} \quad (2.127)$$

If we assume that the heat capacity is independent of temperature and integrate both sides, we get:

$$\bar{C}_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{\bar{V}_1}^{\bar{V}_2} \frac{d\bar{V}}{\bar{V}} \Rightarrow \bar{C}_V \ln \left(\frac{T_2}{T_1} \right) = R \ln \left(\frac{\bar{V}_1}{\bar{V}_2} \right) \quad (2.128)$$

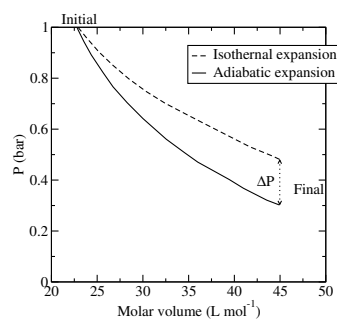
For an ideal gas we have $\bar{C}_P - \bar{C}_V = R$ and thus we can rewrite Eq. (2.128) as:

$$\frac{T_2}{T_1} = \left(\frac{\bar{V}_1}{\bar{V}_2} \right)^{\gamma-1} \text{ where } \gamma = \frac{\bar{C}_P}{\bar{C}_V} \quad (2.129)$$

The same result can be written in alternative forms:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \quad (2.130)$$

$$P_1 \bar{V}_1^\gamma = P_2 \bar{V}_2^\gamma \quad (2.131)$$



Isothermal and reversible adiabatic expansions of one mole of an ideal monoatomic gas. The isothermal case results in higher pressure in the end because there is heat transfer to the system from the surroundings (to keep the temperature constant). In the adiabatic case the temperature decreases during expansion.

Example. Consider an adiabatic, reversible expansion of 0.020 mol Ar (ideal gas), initially at 25 °C, from 0.50 L to 1.00 L. What is the final temperature and how much work is done?

Solution. First we have to modify Eq. (2.129):

$$T_2 = T_1 \left(\frac{\bar{V}_1}{\bar{V}_2} \right)^{\gamma-1}$$

Substituting the values, we get the final T_2 (see Eqs. (2.119) and (2.120)):

$$T_2 = (298 \text{ K}) \times \left(\frac{0.50 \text{ L}}{1.00 \text{ L}} \right)^{0.666} = 188 \text{ K}$$

From the temperature difference we can calculate the work ($\bar{C}_V = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$; ideal gas):

$$\begin{aligned} w_{rev} &= n\bar{C}_V\Delta T \\ &= (0.020 \text{ mol}) \times (12.47 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times (-110 \text{ K}) = -27 \text{ J} \end{aligned}$$

Note the sign: the gas does work.

2.11 Thermochemistry

Chemical reaction (or phase change) in a system is said to be:

Exothermic, if heat $q < 0$ (i.e. it releases heat).

Endothermic, if heat $q > 0$ (i.e. it requires heat).

Since enthalpy is an extensive property that is a function of the state of the system (homogenous of degree 1; see Eq. (1.42)), we can express it in terms of partial molar enthalpies:

$$dH = \sum_{i=1}^{N_s} \bar{H}_i dn_i \quad (2.132)$$

where N_s is the number of species and H_i is the molar enthalpy of species i . When the temperature and the pressure are constant, Eq. (2.109) gives:

$$dH = dq_P = \sum_{i=1}^{N_s} \bar{H}_i dn_i \quad (2.133)$$

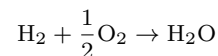
where subscript P refers to constant pressure.

Notation of chemical reactions:

$$0 = \sum_{i=1}^{N_s} v_i B_i \quad (2.134)$$

where B_i is the chemical formula of species i and v_i is the corresponding stoichiometric coefficient.

Example. Use the above notation to express the following chemical reaction:



Solution. Insert the stoichiometric coefficients into Eq. (2.134):

$$0 = -1\text{H}_2 - \frac{1}{2}\text{O}_2 + 1\text{H}_2\text{O}$$

Here $v_1 = -1, v_2 = -1/2, v_3 = 1$ and $N_s = 3$.

Extent of chemical reaction (ξ) is defined as:

$$n_i = n_{i0} + v_i \xi \quad (2.135)$$

where n_{i0} is the initial amount of species i (mol), ξ is the extent of reaction (mol) and v_i are the stoichiometric coefficients (dimensionless). Note that ξ evolves from initial value of zero to the final value where any of the component n_i 's reach zero.

By combining Eqs. (2.133) and (2.135) we get:

$$dH = dq_P = \sum_{i=1}^{N_s} \bar{H}_i \underbrace{v_i d\xi}_{=dn_i} \quad (2.136)$$

Dividing both sides of this equation by $d\xi$ yields:

$$\Delta_r H = \left(\frac{\partial H}{\partial \xi} \right)_{T,P} = \frac{dq_P}{d\xi} = \sum_{i=1}^{N_s} v_i \bar{H}_i \quad (2.137)$$

where $\Delta_r H$ is the reaction enthalpy. Reaction enthalpy tells us the rate of enthalpy change at given point of reaction (ξ). Note that *the reaction enthalpy depends on the way the chemical equation is written*. For example, $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ has twice the reaction enthalpy than $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$. The SI unit of reaction enthalpy is J mol^{-1} .

Thermodynamic standard state:

Denoted by superscript $^\circ$ (degree). For a standard state, Eq. (2.137) reads:

$$\Delta_r H^\circ = \sum_{i=1}^{N_s} v_i \bar{H}_i^\circ \quad (2.138)$$

The standard state of a substance at a specified temperature is its pure form at 1 bar.

The phase of the substance is indicated by g (gas), l (liquid) or s (solid).

Example. What is the standard state of $\text{CH}_3\text{CH}_2\text{OH}$ (l) at 298 K?

Solution. The standard state is pure liquid ethanol at 298 K and 1 bar (external) pressure.

Enthalpy change in chemical reactions:



Antoine Lavoisier,
French scientist
(1743 - 1794)



Pierre-Simon
Laplace, French
mathematician
and astronomer
(1749 - 1827)

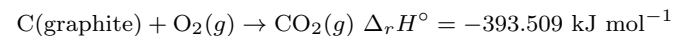
Lavoisier & Laplace in 1780: “The heat absorbed in decomposing a compound must be equal to the heat evolved in its formation under the same conditions.”

This means that in forward and reverse reactions the *sign* in ΔH is changed.

Germain Hess in 1840: “The overall heat of a chemical reaction at constant pressure is the same, regardless of the intermediate steps involved.”

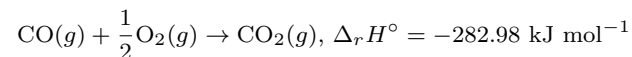
Note that both previous statements follow directly from the first law of thermodynamics.

Example. Burning of graphite (in presence of excess O_2) to CO_2 :

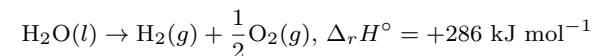


Note that the sign signifies that the reaction is exothermic (releases heat to the surroundings).

Example. Burning of CO (in presence of excess O_2) to CO_2 :



Example. Dissociation of water to hydrogen and oxygen:

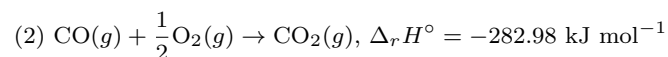
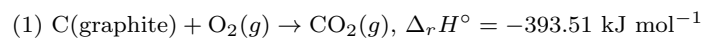


Note that the “+” sign means that the reaction is endothermic (draws heat from the surroundings).

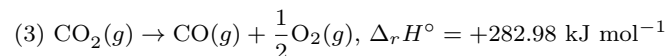
For reactions, that cannot be studied directly, reaction enthalpies can be obtained by dividing the reaction into parts, which can be studied with the desired accuracy.

Example. The heat released by burning graphite to CO is difficult to measure accurately because part of it might produce CO₂ and part of the graphite might not react at all. How can we determine the reaction enthalpy in this case?

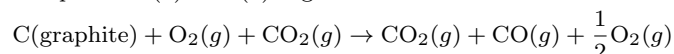
Solution. First we write reactions for burning of graphite yielding CO₂ and burning of CO to CO₂ (excess O₂ to ensure that reactions proceed all the way):



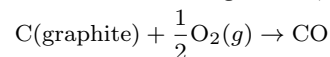
Consider the reverse reaction of the last equation (Lavoisier & Laplace):



Next we add equations (1) and (3) together:



and after cancelling terms from the left and right sides, we get:



The total reaction enthalpy is obtained by adding the corresponding values for the partial reactions (Hess): $\Delta_r H^\circ = (-393.51 + 282.98) \text{ kJ mol}^{-1} = -110.53 \text{ kJ mol}^{-1}$.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ ↺ 🔍 ↻

2.12 Enthalpy of formation

Recall that we don't usually know the absolute values for the internal energy U but only changes in it. Since $H = U + PV$, the same applies for H and therefore we usually just concentrate on changes in enthalpy. However, we can specify a reference state and consider differences in enthalpy from this state (relative enthalpies or enthalpies of formation; $\Delta_f H^\circ$). Such a state is obtained from the stoichiometric amounts of the molecules in the given substance in the standard state and at the temperature under consideration. When enthalpy of formation is calculated, one mole of the product must be considered.

Example. What are the enthalpies of formation ($\Delta_f H^\circ$) for CO₂(g), CO(g), C(g) and O(g) under standard conditions (25 °C and 1 bar) and why?

Solution. Consider first CO₂(g). The formation reaction for CO₂ is: C(s) + O₂(g) → CO₂(g) with $\Delta_f H^\circ = -393.51 \text{ kJ mol}^{-1}$. Note that always for the formation reaction: $\Delta_f H^\circ = \Delta_r H^\circ$. The situation for CO is analogous. How about C(g)? In this case the formation reaction is: C(graphite) → C(g). The reaction enthalpy for this reaction is 716.7 kJ mol⁻¹ under the present conditions (Numerical data can be found from the NIST Chemistry Webbook).

When the enthalpies of formation for each substance in a chemical reaction are known, it is possible to calculate the reaction enthalpy by (both enthalpies under the same conditions):

$$\Delta_r H^\circ = \sum_{i=1}^{N_s} v_i \Delta_f H_i^\circ \quad (2.139)$$

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ ↺ 🔍 ↻

Enthalpy of formation for a compound can be determined:

1. Experimentally: Calorimetric measurements, temperature variations of equilibrium constants, spectroscopic determination of dissociation energies.
2. Theoretically: From the first principles using electron structure methods.

Note: The first law of thermodynamics cannot determine if the reaction will occur spontaneously or not.

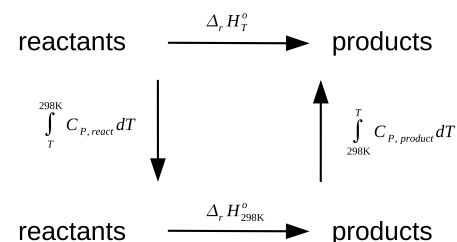
Example. What are the standard enthalpy changes at 298.15 K for the following reaction:



Solution. First we note that for graphite $\Delta_f H^\circ(\text{graphite}) = 0$ (choice of reference point). The other $\Delta_f H^\circ$ values can be looked up from the NIST *chemistry webbook* database: $\Delta_f H^\circ(\text{CO}) = -110.5 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$. Note that these values are given at 298.15 K temperature. The standard reaction enthalpy is now given by:

$$\begin{aligned}\Delta_r H^\circ &= 2\Delta_f H^\circ(\text{CO}) - \Delta_f H^\circ(\text{CO}_2) - \Delta_f H^\circ(\text{C}(\text{graphite})) \\ &= 2(-110.5 \text{ kJ mol}^{-1}) - (-393.5 \text{ kJ mol}^{-1}) \\ &= 172.5 \text{ kJ mol}^{-1}\end{aligned}$$

If we need to calculate reaction enthalpies at some other temperature than 298.15 K, we have to use heat capacity C_P to account for the change in temperature (Kirchhoff's law):



Starting from the reactants, calculate the change in enthalpy when temperature is changed from T to 298 K, use the known reaction enthalpy for the reaction, and calculate the change in enthalpy when temperature is changed back from 298 K to T .

The expression for $\Delta_r H^\circ$ at the given temperature T is therefore:

$$\Delta_r H_T^\circ = \underbrace{-\int_{298\text{ K}}^T \dots}_{298\text{ K}} + \Delta_r H_{298\text{ K}}^\circ + \int_{298\text{ K}}^T C_{P,\text{product}}^\circ(T) dT \quad (2.140)$$

$$\Delta_r H_T^\circ = \Delta_r H_{298\text{ K}}^\circ + \int_{298\text{ K}}^T \overbrace{\Delta_r C_P^\circ(T)}^{\equiv C_{P,\text{product}}^\circ - C_{P,\text{react}}^\circ} dT \quad (2.141)$$

$$\Delta_r C_P^\circ(T) = \sum_{i=1}^{N_s} v_i \bar{C}_{P,i}^\circ(T) \quad (\text{total heat capacity change in the reaction}) \quad (2.142)$$

To get the temperature dependency of the reaction heat capacity ($\Delta_r C_P^\circ$), we use the empirical form of Eq. (2.114):

$$\Delta_r C_P^\circ = \Delta_r \alpha + (\Delta_r \beta) T + (\Delta_r \gamma) T^2 \quad (2.143)$$

$$\text{with } \Delta_r \alpha = \sum_{i=1}^{N_s} v_i \alpha_i, \Delta_r \beta = \sum_{i=1}^{N_s} v_i \beta_i \text{ and } \Delta_r \gamma = \sum_{i=1}^{N_s} v_i \gamma_i$$

If the values α , β and γ for each species i are known, it is possible to insert them into Eq. (2.143) and further use Eq. (2.142) to obtain the reaction heat capacity:

$$\begin{aligned} \Delta_r H_T^\circ &= \Delta_r H_{298\text{ K}}^\circ + \int_{298\text{ K}}^T [\Delta_r \alpha + \Delta_r \beta T + \Delta_r \gamma T^2] dT \quad (2.144) \\ &= \Delta_r H_{298\text{ K}}^\circ + \Delta_r \alpha (T - 298.15\text{ K}) + \frac{\Delta_r \beta}{2} (T^2 - (298.15\text{ K})^2) \\ &\quad + \frac{\Delta_r \gamma}{3} (T^3 - (298.15\text{ K})^3) \end{aligned}$$

In principle, it would be possible to choose another reference temperature. Sometimes absolute zero temperature is used ($\Delta_r H_0^\circ$). For a diatomic molecule, this would correspond to the bond dissociation energy. Note that other empirical parametrizations are often also used. For example, the NIST chemistry webbook uses the Shomate equation, which is essentially a 3rd order polynomial with a $1/T^2$ term added.

Example. The standard enthalpy of formation of gaseous H_2O at 298 K is $-241.8 \text{ kJ mol}^{-1}$ (constants obtained from the NIST chemistry webbook). Estimate its value at 373 K given the following values for the molar heat capacities at constant pressure: $\text{H}_2\text{O (g)}$: $\approx 34 \text{ J K}^{-1} \text{ mol}^{-1}$; $\text{H}_2 \text{ (g)}$: $28.8 \text{ J K}^{-1} \text{ mol}^{-1}$; $\text{O}_2 \text{ (g)}$: $28.9 \text{ J K}^{-1} \text{ mol}^{-1}$. Assume that the heat capacities are independent of temperature.

Solution. The reaction is: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$. When the heat capacities are independent of temperature, Eq. (2.141) can be replaced with:

$$\Delta_r H_{373 \text{ K}}^\circ = \Delta_r H_{298 \text{ K}}^\circ + \underbrace{((373 \text{ K}) - (298 \text{ K}))}_{\Delta T = 75 \text{ K}} \Delta_r C_P^\circ$$

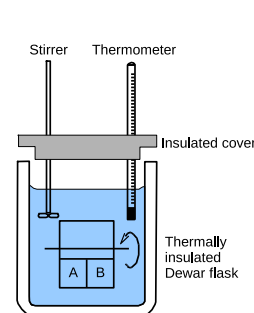
To proceed, we need to evaluate $\Delta_r C_P^\circ$:

$$\begin{aligned} \Delta_r C_P^\circ &= C_{P, \text{H}_2\text{O}(\text{g})}^\circ - \left(C_{P, \text{H}_2(\text{g})} + \frac{1}{2} C_{P, \text{O}_2(\text{g})}^\circ \right) \\ &= 34 \text{ J K}^{-1} \text{ mol}^{-1} - \left(28.8 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{1}{2} \times 28.9 \text{ J K}^{-1} \text{ mol}^{-1} \right) \\ &= -9.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Using this we can calculate $\Delta_r H_{373 \text{ K}}^\circ$:

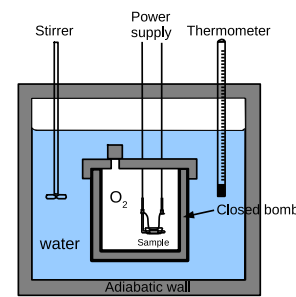
$$\Delta_r H_{373 \text{ K}}^\circ = -241.8 \text{ kJ mol}^{-1} + (75 \text{ K}) \times (-9.4 \text{ J K}^{-1} \text{ mol}^{-1}) \approx -243 \text{ kJ mol}^{-1}$$

2.13 Calorimetry



Constant pressure calorimeter. Experimental determination of ΔH .

When reactants A and B are mixed in the calorimeter, heat is either released or absorbed. This is observed using a thermometer. Note: PV -work is possible.



Constant volume calorimeter. Experimental determination of ΔU .

A compound reacts with O_2 (combustion). The heat released from the reaction, is conducted to the surrounding water bath. Changes in the bath temperature are measured with a thermometer. Note: no PV -work is possible.

Constant pressure calorimeter: Chemical reaction: $R \rightarrow P$ (volume may change).

$$\Delta H_A = \Delta H(T_1) + \Delta H_P \quad (2.145)$$

$$\Delta H_A = \Delta H_R + \Delta H(T_2) \quad (2.146)$$

where ΔH_A is the overall enthalpy change.

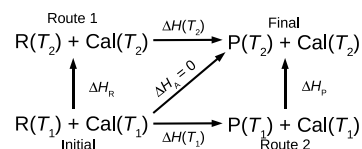
The overall enthalpy is *conserved*: $\Delta H_A = 0$. Thus we have two equations for ΔH at T_1 or T_2 (ΔT small; see Eq. (2.112) with $\Delta P = 0$):

$$\Delta H(T_1) = -\Delta H_P = -\overbrace{[C_P(P) + C_P(\text{Cal})]}^* (T_2 - T_1) = -C_{P,eff}(P)\Delta T \quad (2.147)$$

$$\Delta H(T_2) = -\Delta H_R = -\underbrace{[C_P(R) + C_P(\text{Cal})]}_{**} (T_2 - T_1) = -C_{P,eff}(R)\Delta T \quad (2.148)$$

$C_P(P)$ = (constant pressure) heat capacity of the product.
 $C_P(R)$ = (constant pressure) heat capacity of the reactant.
 $C_P(\text{Cal})$ = (constant pressure) heat capacity of the calorimeter.

Note: All C_P 's above are extensive variables (i.e. *not* molar quantities). In practice, $C_P(\text{cal})$ dominates and $C_{P,eff}(P) \approx C_{P,eff}(R)$.



Two different ways to proceed from reactants to products.

If ΔH has been determined in a calorimetric experiment, $\Delta_r H$ for a balanced chemical reaction can be calculated using:

$$\Delta_r H = \frac{\Delta H}{\Delta \xi} \quad (\xi = \text{the extent of reaction; see Eq. (2.135)}) \quad (2.149)$$

If $\Delta \xi \approx 1$ then $\Delta_r H \approx \Delta H$. How can we determine $C_P(\text{cal})$ in Eqs. (2.147) and (2.148)?

Use a calibrated heater to supply heat into the system and observe the temperature change using a thermometer. The amount of heat supplied by the heater is:

$$q = \int_0^t P(t) dt = \underbrace{UI}_{=P} \int_0^t dt = RI^2 t \quad (2.150)$$

$$R = \frac{U}{I} \quad (\text{Ohm's law}) \quad (2.151)$$

$$P = UI \quad (\text{definition of power}) \quad (2.152)$$

where q is the heat supplied by the electrical heater element, P is the power dissipated (constant; Watt), U is the applied potential (Volt; *not internal energy*), I is the current (Ampere) and R is the heater resistance (Ohm). Alternatively, a reference chemical reaction with known heat release can be used.

By recording data on q vs. T , it is possible to obtain the total heat capacity from the slope, $\Delta q/\Delta T$, of this graph.

Constant volume calorimeter: Chemical reaction: $R \rightarrow P$ (pressure may change).
At constant volume ($\Delta V = 0$), there cannot be any PV -work. This means that:

$$P\Delta V = 0 \quad (2.153)$$

Eq. (2.102) states that:

$$\Delta U = C_V \Delta T \quad (2.154)$$

when ΔT is small (such that C_V is independent of T). Analogously to Eqs. (2.147) and (2.148) we have:

$$\Delta U(T_1) = -\Delta U_P = -[C_V(P) + C_V(\text{Cal})](T_2 - T_1) = -C_{V,eff}(P)\Delta T \quad (2.155)$$

$$\Delta U(T_2) = -\Delta U_R = -[C_V(R) + C_V(\text{Cal})](T_2 - T_1) = -C_{V,eff}(R)\Delta T \quad (2.156)$$

The molar quantity is given by:

$$\Delta_r U = \frac{\Delta U}{\Delta \xi} \quad (2.157)$$

The difference between $\Delta_r H$ and $\Delta_r U$ is the PV -work. For an ideal gas this is given by (N_s is the number of gaseous components, $T \approx$ constant, $v_i = \Delta n_i / \Delta \xi$):

$$\Delta_r H = \Delta_r U + \frac{\Delta(PV)}{\Delta \xi} \approx \Delta_r U + RT \sum_{i=1}^{N_s} v_{g,i} \quad (2.158)$$

where $v_{g,i}$ is the stoichiometric coefficient for gaseous product i (solids and liquids do not contribute).

Notes:

- ▶ In most experiments $C(\text{Cal})$ is large compared to $C(R)$ or $C(P)$, which simply gives $\Delta U = -C_V(\text{Cal})\Delta T$ or $\Delta H = -C_P(\text{Cal})\Delta T$.
- ▶ Most chemists are interested in enthalpies because they describe best chemical reactions in open vessels. Theoretical chemists, however, would be more interested in internal energy because it is more directly related to the energies of bond forming/breaking.

Example. If we pass a current of 10.0 A from a 12 V power supply for 300 s, what is the amount of heat supplied?

Solution. The amount of heat dissipated by the heater is given by $q = UIt$:

$$q = (10.0 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) = 3.6 \times 10^4 \underbrace{\text{AVs}}_{=\text{J}} = 36 \text{ kJ}$$

Example. If 1.247 g of solid glucose is burned in an adiabatic bomb calorimeter ($\Delta U = -2801 \text{ kJ mol}^{-1}$), the temperature rises 1.693 K. What is the effective heat capacity of the bomb calorimeter?

Solution. Since the volume is constant, we have:

$$\Delta U = -C_V(\text{Cal})\Delta T \Rightarrow C_V(\text{Cal}) = -\frac{\Delta U}{\Delta T}$$

$$C_V(\text{Cal}) = - (1.247 \text{ g}) \times \frac{1 \text{ mol}}{180.16 \text{ g}} \times \frac{-2801 \text{ kJ}}{1 \text{ mol}} / (1.693 \text{ K}) = 11.44 \text{ kJ K}^{-1}$$

Example. Consider an adiabatic bomb calorimeter. When compounds change their phase (e.g. from solid to gas or liquid to gas) during the reaction, the effective volume of the calorimeter changes. Assuming that the resulting gas products behave according to the ideal gas law, what is the correction required for the change in ΔH due to PV -work?

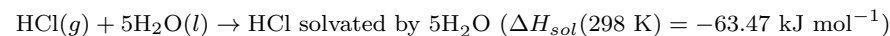
Solution. If gaseous components are produced or consumed, the pressure inside the calorimeter changes during the reaction. This causes ΔU and ΔH to deviate from each other. This difference can be approximately expressed as:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) \approx \Delta U + RT \times \Delta n$$

where we assume that the change in temperature is small. This correction is rather small and typically less than 1 %.

Several types of processes can be considered by calorimetric methods:

Solvation process:



Neutralization process: $\text{H-A} + \text{HO-B} \rightarrow \text{H}_2\text{O} + \text{A}^- + \text{B}^+$

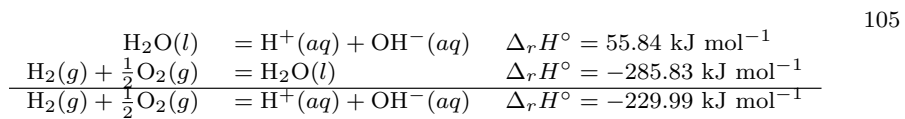
For example, A could be Cl and B Na. When strong acid/base combination is neutralized, the enthalpy difference is approximately constant and independent of the base/acid pair. The reason is that the main contribution to the enthalpy difference (heat of neutralization) originates from:



When a dilute solution of weak acid/base is neutralized, the heat of neutralization is less than that of strong acid/base neutralization.

Example. Calculate the enthalpy of formation of H^+ and OH^- .

Solution. We use the known reactions to deduce the enthalpy of formation:



Note: Separate enthalpies of formation cannot be obtained for H^+ and OH^- , only their sum. In most tablebooks, for H^+ the associated $\Delta_f H^\circ$ has been assigned to zero.

Chapter 3: Second and third laws of thermodynamics

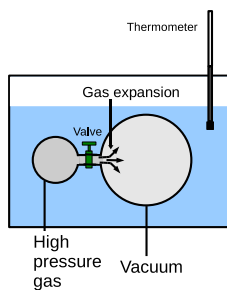
“The entropy of the universe tends to a maximum.”

3.1 Entropy as a state function

107

The first law of thermodynamics says only that the total energy is conserved but *it does not provide any information as to whether the process can proceed spontaneously*.

Example. Consider gas expanding into vacuum. In practice, we know that the gas will flow from the high pressure chamber into the low pressure chamber.



The first law for this system only states that the total energy is conserved but says nothing about which way the gas would flow.

108

Example. In practice, we know that some chemical reaction proceed *spontaneously* but some may require heat in order to proceed (*nonspontaneous process*)

Question: How do we identify a spontaneous process?

From the previous examples, it is obvious that a flow of heat is involved in these processes. Heat is, however, not a state function (i.e. dq is not an exact differential). This can be seen by inspecting Eq. (2.98):

$$dq_{rev} = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV \quad (3.159)$$

where we consider reversible heating and $P_{ext} = P$. We will use Eq. (2.67) as the test for exactness:

$$M = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{and} \quad N = P + \left(\frac{\partial U}{\partial V} \right)_T \quad (3.160)$$

and the required partial derivatives are then (U is well behaving, i.e. derivatives exist and are continuous):

$$\begin{aligned} \left(\frac{\partial M}{\partial V} \right)_T &= \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_V \\ \left(\frac{\partial N}{\partial T} \right)_V &= \left(\frac{\partial P}{\partial T} \right)_V + \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_V \end{aligned} \quad (3.161)$$

Subtracting the two partial derivatives gives:

$$\left(\frac{\partial N}{\partial T}\right)_V - \left(\frac{\partial M}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (3.162)$$

Based on this dq_{rev} would only be exact if $\left(\frac{\partial P}{\partial T}\right)_V = 0$. *This does not hold even for ideal gases:* $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$ (from $PV = nRT$). Thus line integral of dq_{rev} depends on the path and q_{rev} is not a state function of the system. Thus it is not useful to consider heat as an indicator for a spontaneity of the process.

Recall that some times division of an inexact differential by a suitable term (integrating factor) may result in exact differential. In this case it turns out that division by T (temperature) yields an exact differential:

$$\frac{dq_{rev}}{T} = \underbrace{\frac{(\partial U/\partial T)_V}{T}}_{=M} dT + \underbrace{\left[\frac{P}{T} + \frac{(\partial U/\partial V)_T}{T}\right]}_{=N} dV \quad (3.163)$$

By taking the partial derivatives required in the exactness test and subtracting $(\partial M/\partial V)_T$ from $(\partial N/\partial T)_V$ (denoted by Δ) we get:

$$\Delta = \frac{1}{T} \left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T^2} - \frac{1}{T^2} \left(\frac{\partial U}{\partial V}\right)_T \quad (3.164)$$

At least for ideal gases $\Delta = 0$ since $(\partial U/\partial V)_T = 0$ (Joule's experiment) and $PV = nRT$. Thus dq_{rev}/T is exact for ideal gases.

The above expression for Δ can be derived as follows. First calculate $(\partial N/\partial T)_V$:

$$\begin{aligned} \left(\frac{\partial N}{\partial T}\right)_V &= \left(\frac{\partial}{\partial T} \left(\frac{P}{T}\right)\right)_V + \left(\frac{\partial}{\partial T} \left(\frac{1}{T} \times \left(\frac{\partial U}{\partial V}\right)_T\right)\right)_V \\ &= \frac{1}{T} \left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T^2} + \left(\frac{\partial}{\partial T} \left(\frac{1}{T} \times \left(\frac{\partial U}{\partial V}\right)_T\right)\right)_V \\ &= \frac{1}{T} \left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T^2} - \frac{1}{T^2} \times \left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T} \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \end{aligned}$$

Next we calculate $(\partial M/\partial V)_T$:

$$\begin{aligned} \left(\frac{\partial M}{\partial V}\right)_T &= \left(\frac{\partial}{\partial V} \left(\frac{1}{T} \times \left(\frac{\partial U}{\partial T}\right)_V\right)\right)_T \\ &= \frac{1}{T} \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \end{aligned}$$

Subtracting the first expression from the second gives the difference Δ :

$$\Delta = \frac{1}{T} \left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T^2} - \frac{1}{T^2} \left(\frac{\partial U}{\partial V}\right)_T$$

It will turn out that the dq_{rev}/T is the quantity that we are looking for (entropy). It is a useful quantity because it is a state function of the system (no path dependency). Note that we have only shown this to hold for ideal gases, a more detailed consideration will be given later.

Example. Show that the values of the line integral for dq_{rev}/T are identical along the following paths (monoatomic ideal gas, reversible processes, $n = 1$):

Closed path 1:

Segment A: $(T_1, P_1, V_1) - (T_1, P_2, V_2)$ isothermal

Segment B: $(T_1, P_1, V_1) - (T_2, P_3, V_2)$ adiabatic

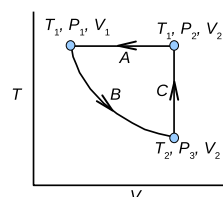
Segment C: $(T_2, P_3, V_2) - (T_1, P_2, V_2)$ constant volume

Closed path 2:

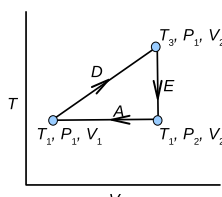
Segment A: $(T_1, P_1, V_1) - (T_1, P_2, V_2)$ isothermal

Segment D: $(T_1, P_1, V_1) - (T_3, P_1, V_2)$ constant pressure

Segment E: $(T_3, P_1, V_2) - (T_1, P_2, V_2)$ constant volume



Closed path #1



Closed path #2

Solution. Calculate dq_{rev}/T along each segment. And sum the contributions from each segment.

Path 1. (“contribution from A + B + C = 0”)

Segment A: The temperature is constant along this path. For an ideal gas, the internal energy depends only on the temperature (Eq. (2.117)) and therefore $dU = 0$. Hence along this path (Eq. (2.64)): $dq_{rev} = -dw = PdV = (RT/V)dV$. Division of both sides by T and integration gives:

$$\Delta S = \int_{q_2}^{q_1} \frac{dq_{rev}}{T} = R \int_{V_2}^{V_1} \frac{dV}{V} = R \ln \left(\frac{V_1}{V_2} \right)$$

Segment B: Since the change is adiabatic, $dq_{rev} = 0$ and the corresponding line integral over dq_{rev}/T is zero as well.

Segment C: Because volume is constant (“constant volume process”), $dw_{rev} = 0$. The first law (Eqs. (2.64) and (2.100)) now states that $dq_{rev} = dU = C_V dT$. Division by T and integration along the segment gives:

$$\Delta S = \int_{q_3}^{q_2} \frac{dq_{rev}}{T} = \int_{T_2}^{T_1} \frac{C_V}{T} dT = C_V \int_{T_2}^{T_1} \frac{dT}{T} = C_V \ln \left(\frac{T_1}{T_2} \right)$$

Note that C_V is independent of temperature (ideal gas; Eq. (2.119)).

113

Summing along the path B + C gives just $C_V \ln(T_1/T_2)$ and the contribution along A is $R \ln(V_2/V_1)$. Thus we have (using Eq. (2.128)):

$$\oint dS = \oint \frac{dq_{rev}}{T} = C_V \ln\left(\frac{T_1}{T_2}\right) - R \ln\left(\frac{V_2}{V_1}\right) = 0$$

Note that an alternative form for Eq. (2.128) is (considering now segment B):

$$\left(\frac{T_1}{T_2}\right) = \left(\frac{V_2}{V_1}\right)^{R/C_V}$$

Path 2. (“contribution from D + E + A = 0”)

Segment A: The same as in the previous path.

Segment D: At constant pressure $dq_{rev}/T = dH/T$ (Eq. (2.109)). According to Eq. (2.112), $dH/T = (C_P/T)dT$. Integration of the expression from T_1 to T_3 gives (C_P is constant for ideal gases; Eq. (2.120)):

$$\Delta S = \int_{q_1}^{q_3} \frac{dq_{rev}}{T} = \int_{T_1}^{T_3} \frac{C_P}{T} dT = C_P \ln\left(\frac{T_3}{T_1}\right)$$

Segment E: At constant volume, $dw = 0$. The first law of thermodynamics then gives (Eqs. (2.64) and (2.100)):

$$\Delta S = \int_{q_3}^{q_1} \frac{dq_{rev}}{T} = \int_{U_3}^{U_1} \frac{dU}{T} = \int_{T_3}^{T_1} \frac{C_V}{T} dT = C_V \ln\left(\frac{T_1}{T_3}\right) \quad (\text{constant } C_V \text{ assumed})$$

The total contribution over the closed loop along “D + E + A” segments is:

$$\begin{aligned} \oint dS &= \oint \frac{dq_{rev}}{T} = C_P \ln\left(\frac{T_3}{T_1}\right) + C_V \ln\left(\frac{T_1}{T_3}\right) - R \ln\left(\frac{V_2}{V_1}\right) \\ &= \ln\left(\frac{T_3}{T_1}\right) \times \underbrace{(C_P - C_V)}_{=R \text{ (Eqs. (2.119, 2.120))}} - R \ln\left(\frac{V_2}{V_1}\right) \\ &= R \times \left(\ln\left(\frac{T_3}{T_1}\right) - \ln\left(\frac{V_2}{V_1}\right) \right) \end{aligned}$$

In order to proceed, we note that the pressure at the end points of segment D is constant. By using the ideal gas law for both end points, we get:

$$\frac{T_3}{T_1} = \frac{V_2}{V_1}$$

Thus the logarithm terms cancel and the integral is zero.

3.2 The second law of thermodynamics

115

Definition of entropy (S):

$$dS = \frac{dq_{rev}}{T} \quad (3.165)$$

$$\Delta S = \int \frac{dq_{rev}}{T} \quad (3.166)$$

Integration of entropy over closed loops yield zero because dS is an exact differential (S is a state function):

$$\oint \frac{dq_{rev}}{T} = \oint dS = 0 \quad (3.167)$$

In general, we have the following inequality (i.e. dq reversible or irreversible):

$$0 = \oint dS = \oint \frac{dq_{rev}}{T} \geq \oint \frac{dq}{T} \quad (3.168)$$

The inequality can also be written in differential form:

$$dS \geq \frac{dq}{T} \quad (3.169)$$

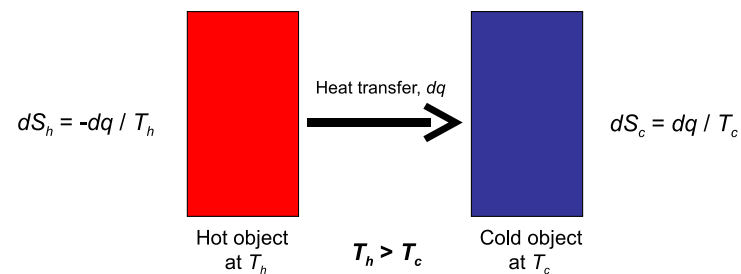
For an isolated system, the inequality simplifies to:

$$dS \geq 0 \quad (3.170)$$



Rudolph Clausius,
German physicist and
mathematician (1822 -
1888)

The idea behind Clausius inequality (3.170) can be understood by considering the following example:



$$dS = dS_c + dS_h = dq \times \left(\frac{1}{T_c} - \frac{1}{T_h} \right) \geq 0 \quad (3.171)$$

Thus we conclude that in presence of spontaneous (irreversible) processes we have $dS > 0$. At thermal equilibrium we would have $T_h = T_c$ and $dS = 0$. We will return to justification of Eq. (3.169) later (non-isolated system).

116

The second law of thermodynamics consists of two statements:

1. There is a state function called the entropy S that can be calculated from $dS = dq_{rev}/T$.
2. The change in entropy in any process is given by $dS \geq dq/T$, where the ' $>$ ' sign applies to a spontaneous (irreversible; dq_{irrev}) process and the equality for a reversible process (dq_{rev}). In order to calculate ΔS , one must use a reversible process.

Justification for the Clausius inequality $dS \geq \frac{dq}{T}$ (Eq. (3.169)):

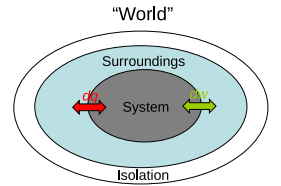
1. If the process is reversible then by definition $dS = \frac{dq_{rev}}{T}$.
2. If the process is irreversible, we need to show that $dS > \frac{dq_{irrev}}{T}$. Consider only PV -work and then the 1st law is $dU = dq - P_{ext}dV$. For a reversible process this gives: $dU = dq_{rev} - PdV$ and for an irreversible process: $dU = dq_{irrev} - P_{ext}dV$. Since dU is exact, the previous dU 's must be equal (consider integration over short paths): $dq_{rev} - PdV = dq_{irrev} - P_{ext}dV$. Rearranging gives: $dq_{rev} - dq_{irrev} = (P - P_{ext})dV$. If $P - P_{ext} > 0$ the system will expand spontaneously and $dV > 0$. If $P - P_{ext} < 0$ the system will contract spontaneously and $dV < 0$. In both cases $dq_{rev} - dq_{irrev} > 0$. Dividing both sides by T gives $\frac{dq_{rev}}{T} - \frac{dq_{irrev}}{T} > 0$. By using the definition of entropy (Eq. (3.165)) we get: $dS > \frac{dq_{irrev}}{T}$.

Another way to state the 2nd law of thermodynamics: "The entropy increases in a spontaneous process in an isolated system". The entropy increases as long as spontaneous processes proceed. When the system does not change any more, the entropy will have its maximum value and we have $dS = 0$. *The entropy change tells us whether a process or chemical reaction can occur spontaneously in an isolated system.* Consider an isolated system (consisting of system and surroundings):

System (at T_{syst}) and surroundings (at T_{surr}):

$$dS_{total} = dS_{syst} + dS_{surr}$$

$$dq_{total} = dq_{syst} + dq_{surr} = 0 \Rightarrow dq_{syst} = -dq_{surr}$$



The total entropy cannot decrease: $dS_{total} = dS_{syst} + dS_{surr} \geq 0$ (Eq. (3.170)). For the system we have: $dS_{syst} = dq/T_{syst}$ and for the surroundings: $dS_{surr} = -dq/T_{surr}$. Therefore we have:

$$dS_{syst} \geq \frac{dq}{T_{surr}} \quad (3.172)$$

Note: The equal sign case only applies for reversible processes in Eq. (3.172). The equal sign would also then apply in $dS_{total} = dS_{syst} + dS_{surr} = 0$ (reversible process).

Based on changes in entropy, we can identify three different cases:

- (1) $dS > dq/T$ spontaneous (irreversible) process (3.173)
- (2) $dS = dq/T$ reversible process (“nearly equilibrium”)
- (3) $dS < dq/T$ impossible process (“forced process”)

For an isolated system ($dq = 0$), we have:

- (1) $dS > 0$ spontaneous (irreversible) process (3.174)
- (2) $dS = 0$ reversible process (“nearly equilibrium”)
- (3) $dS < 0$ impossible process (“forced process”)

Because S is a state function, it can be integrated between any two states of the system:

$$\int_{S_1}^{S_2} dS = \int_{q_1}^{q_2} \frac{dq_{rev}}{T} = S_2 - S_1 = \Delta S \quad (3.175)$$

The integration path in Eq. (3.175) must be reversible. This equation can be applied to irreversible processes only if a path consisting of reversible segments, can be constructed. Note that there is no entropy change for a reversible adiabatic process.

Example. Is the expansion of a monoatomic ideal gas into a larger volume thermodynamically spontaneous? More specifically, consider reversible and isothermal expansion of an isolated ideal gas ($n = 1$ mol) initially at 298 K into a volume that is twice as large as its initial volume.

Solution. Recall from Eq. (2.85) that the reversible work done is ($n = 1$ mol):

$$w_{rev} = - \int_{V_1}^{V_2} P_{ext} dV = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \left(\frac{V_2}{V_1} \right) = -RT \ln(2)$$

The internal energy of a monoatomic ideal gas does not depend on volume (Eq. (2.117)). Thus we have $\Delta U = q_{rev} + w_{rev} = 0$ and further $q_{rev} = -w_{rev} = RT \ln(2)$. Eq. (3.166) with constant T states that $\Delta S = \frac{q_{rev}}{T} = R \ln(2) > 0$ where we used the fact that $V_2 = 2 \times V_1$. Because the entropy change is positive, the change is spontaneous (as we already knew in practice). For the reverse process we would have $\Delta S < 0$, which means that it does not happen (unless forced).

Note: The previous problem has nothing to do with minimizing the energy, which is constant during the process. The process is purely entropy driven and is related to decrease in “order” at larger volume. By order we mean the arrangement of atoms or molecules. For example, $S_{gas} > S_{liquid} > S_{solid}$.

Example. Calculate the entropy change when argon at 25 °C and 1.00 atm in a container of volume 500 cm³ is allowed to expand to 1000 cm³. Assume that argon behaves according to the ideal gas law.

Solution. From the ideal gas law we can calculate the amount of substance:

$$n = \frac{PV}{RT} = 0.0204 \text{ mol}$$

In previous example we had $n = 1$. If the same calculation is carried out with n in place, we have:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) = nR \ln(2) = 0.118 \text{ J K}^{-1}$$

3.3 Entropy changes in reversible processes

Consider a constant temperature (T) and pressure (P) process. Now we can apply both Eqs. (2.109)) and (3.175), respectively:

$$\begin{aligned} \Delta H &= q_{rev} \text{ and } \Delta S = \frac{q_{rev}}{T} \\ \Rightarrow \Delta S &= \frac{\Delta H}{T} \end{aligned} \quad (3.176)$$

Examples of constant T and P processes are: vaporization of pure liquid into its vapor at the equilibrium vapor pressure (P), sublimation, and structural transitions in solids.

Example. What is the change in molar entropy of n -hexane when it is vaporized at its boiling point (68.7 °C) under atmospheric pressure (1.01325 bar)? The molar enthalpy of vaporization is 28850 J mol⁻¹.

Solution. If n -hexane is vaporized into the saturated vapor at the given temperature, the process is reversible and the molar entropy change is given by Eq. (3.176):

$$\Delta \bar{S} = \frac{\Delta \bar{H}}{T} = \frac{28850 \text{ J mol}^{-1}}{341.8 \text{ K}} = 84.41 \text{ J K}^{-1} \text{ mol}^{-1}$$

Other useful special cases:

Constant V: Using Eq. (2.100) we have:

$$dS = \frac{dq_{rev}}{T} = \frac{C_V dT}{T} \quad (3.177)$$

Integration of dS gives:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT \approx C_V \ln \left(\frac{T_2}{T_1} \right) \quad (3.178)$$

Constant P: Using Eq. (2.112) we get:

$$dS = \frac{dq_{rev}}{T} = \frac{C_P dT}{T} \quad (3.179)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT \approx C_P \ln \left(\frac{T_2}{T_1} \right) \quad (3.180)$$

Constant T and ideal gas: Following our previous ideal gas calculation, we have:

$$dS = \frac{dq_{rev}}{T} = -\frac{dw_{rev}}{T} = \frac{PdV}{T} \quad (3.181)$$

$$\Delta S = \int_{V_1}^{V_2} \frac{P}{T} dV = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \left(\frac{V_2}{V_1} \right) = -nR \ln \left(\frac{P_2}{P_1} \right)$$

In terms of standard pressure and entropy (also molar quantities), the previous expression can be written as:

$$\bar{S} = \bar{S}^\circ - R \ln \left(\frac{P}{P^\circ} \right) \quad (P^\circ = 1 \text{ bar standard pressure}) \quad (3.182)$$

Example. Calculate the entropy change when argon gas at 25 °C and 1.00 atm in container of volume 500 cm³ is allowed to expand to 1000 cm³ and is simultaneously heated to 100 °C. Assume that argon behaves according to the ideal gas law.

Solution. The first part of the process was already considered in a previous example. The entropy change (ΔS) due to volume change was 0.118 J K⁻¹. In the second step the gas is heated from 298 K to 373 K at constant volume (Eq. (3.178)):

$$\Delta S = n\bar{C}_V \ln \left(\frac{T_2}{T_1} \right) = (0.0204 \text{ mol}) \times \left(12.48 \frac{\text{J}}{\text{K mol}} \right) \times \ln \left(\frac{373 \text{ K}}{298 \text{ K}} \right) = 0.057 \text{ J K}^{-1}$$

where C_V was calculated from the relation $\bar{C}_P - \bar{C}_V = R$. The value of \bar{C}_P can be found from the NIST chemistry webbook. Note the handling of the process in two steps. The total change in entropy is the sum of the two: $\Delta S = 0.175 \text{ J K}^{-1}$.

Note: Because S is a state function (dS exact), we can choose any convenient path for integration. In this case it was chosen as: (1) volume change and then (2) temperature change.

Example. Half a mole of an ideal gas expands isothermally and reversibly at 298.15 K from a volume of 10 L to a volume of 20 L. (a) What is the change in the entropy of the gas? (b) How much work is done on the gas? (c) How much heat is transferred to the surroundings (q_{surr})? (d) What is the change in the entropy of the surroundings? (e) What is the change in the total entropy (system + surroundings)?

Solution. (a) Use Eq. (3.181):

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) = (0.5 \text{ mol}) \times (8.3145 \text{ JK}^{-1}\text{mol}^{-1}) \ln(2) = 2.88 \text{ JK}^{-1}$$

In part (b) we use Eq. (2.63) and note that T is constant:

$$\Delta U = w_{rev} + q_{rev} = 0 \Rightarrow w_{rev} = -q_{rev}$$

Now Eq. (3.166) gives:

$$\Delta S = \frac{q_{rev}}{T} \Rightarrow q_{rev} = T\Delta S$$

and further:

$$w_{rev} = -T\Delta S = -nRT \ln \left(\frac{V_2}{V_1} \right) = -(2.88 \text{ JK}^{-1}) \times (298.15 \text{ K}) = -859 \text{ J}$$

To solve (c), we need $q_{syst} = 859 \text{ J}$ as calculated above. The total entropy is conserved ($\Delta S_{tot} = 0$) in a reversible process and thus we have $\Delta S_{syst} = -\Delta S_{surr}$ and $T\Delta S_{syst} = -T\Delta S_{surr}$. Using Eq. (3.166) we have $q_{syst} = -q_{surr}$ and hence $q_{surr} = -859 \text{ J}$.

In (d), just like in (c), the total entropy is conserved and hence $\Delta S_{surr} = -\Delta S_{syst} = -2.88 \text{ J K}^{-1}$.

In (e), the total entropy is conserved: $\Delta S_{tot} = 0$. The system and its environment together can be considered as an isolated system. Also note that the process is *reversible*.

Example. Consider that the expansion in the preceding example occurs irreversibly by simply opening a stopcock and allowing the gas to rush into an evacuated bulb of 10 L volume. (a) What is the change in the entropy of the gas? (b) How much work is done on the gas? (c) What is q_{surr} ? (d) What is the change in the entropy of the surroundings? (e) What is the change in the entropy of the system plus the surroundings?

Solution. (a) The change in entropy is the same as in the previous example. Entropy is a state function (dS exact) and hence its value does not depend on path. (b) Expansion into vacuum does not involve PV -work.

(c) Since no work is involved, no changes in heat are involved (the first law).

(d) No heat exchange with the surroundings, thus the entropy of the surroundings does not change.

(e) $\Delta S_{tot} = \Delta S_{syst} + \Delta S_{surr} = 2.88 \text{ J K}^{-1} + 0 \text{ J K}^{-1} = 2.88 \text{ J K}^{-1}$. Since the process is irreversible, we expect that the total entropy would increase (Eq. (3.172)).

Summary: Calculation of ΔS for various changes in state

In general, we have to find a reversible path in order to apply Eq. (3.166):

$$\Delta S = \int \frac{dq_{rev}}{T}$$

Because S is a state function, the entropy change would then apply for all paths (also for irreversible paths) that have the same initial and final states. Note that dq_{rev} is only defined for reversible paths.

Specific cases for one mole of substance:

Constant V : substance(T_1, V) \leftrightarrow substance(T_2, V)

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT \text{ (Eq. (3.178))}$$

If the constant-volume heat capacity C_V is independent of T :

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right)$$

Constant P : substance(T_1, P) \leftrightarrow substance(T_2, P)

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT \text{ (Eq. (3.180))}$$

If the constant-pressure heat capacity C_P is independent of T :

$$\Delta S = C_P \ln \left(\frac{T_2}{T_1} \right)$$

Phase change at constant T and P : solid(T, P) \leftrightarrow liquid(T, P)
 liquid(T, P) \leftrightarrow gas(T, P)
 solid(T, P) \leftrightarrow gas(T, P)
 $\Delta S = \frac{\Delta H}{T}$ (Eq. (3.176))
 where ΔH is the heat of vaporization, sublimation or fusion (crystallization).

Ideal gas at constant T : ideal gas(P_1, V_1, T) \leftrightarrow ideal gas(P_2, V_2, T)

$$\Delta S = R \ln \left(\frac{V_2}{V_1} \right) = -R \ln \left(\frac{P_2}{P_1} \right) \text{ (Eq. (3.181))}$$

Remember the correct sign for ΔS : $\Delta S > 0$ when the volume increases.

Mixing of two ideal gas systems at constant T and P :

$$n_A \text{ A}(T, P) + n_B \text{ B}(T, P) = n \text{ mixture}(T, P)$$

Here $n = n_A + n_B$. The entropy change due to mixing is given by:

$$\Delta S = -nR (y_A \ln(y_A) + y_B \ln(y_B)) \text{ where } y_A = \frac{n_A}{n_A + n_B}, y_B = \frac{n_B}{n_A + n_B}$$

Note that the entropy change is always positive (see Eq. (3.186)).

Example. Calculate the change in entropy of an ideal monatomic gas B in changing from (P_1, T_1) to (P_2, T_2) .

Solution. First we have to define a reversible path, for which we know how to calculate the entropy change (each segment carried out reversibly):

$$B(T_1, P_1) \rightarrow B(T_2, P_1) \rightarrow B(T_2, P_2)$$

This path has two segments (one where temperature changes and another where pressure changes). For the first step we have:

$$\Delta S = C_P \int_{T_1}^{T_2} \frac{dT}{T} = C_P \ln \left(\frac{T_2}{T_1} \right) = n\bar{C}_P \ln \left(\frac{T_2}{T_1} \right)$$

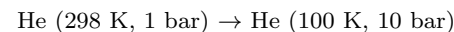
For the second step:

$$\Delta S = -nR \ln \left(\frac{P_2}{P_1} \right)$$

By combining the two:

$$\Delta S = nR \left\{ \ln \left[\left(\frac{T_2}{T_1} \right)^{5/2} \right] - \ln \left(\frac{P_2}{P_1} \right) \right\} \quad (\text{note that } \bar{C}_P = \frac{5}{2}R)$$

Example. Use the result of the previous example to calculate the molar entropy change in the following process:



Solution. Substitute the values to the equation in the previous examples:

$$\Delta \bar{S} = \frac{5}{2}R \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right) = \frac{5}{2} \ln \left(\frac{100 \text{ K}}{298 \text{ K}} \right) - R \ln \left(\frac{10 \text{ bar}}{1 \text{ bar}} \right) = -41.84 \frac{\text{J}}{\text{K mol}}$$

Example. The molar constant-pressure heat capacity of a certain solid at 10 K is $0.43 \text{ J K}^{-1} \text{ mol}^{-1}$. What is the molar entropy at that temperature? Assume that the constant-pressure heat capacity varies as aT^3 where a is a constant.

Solution. Calculate the entropy difference between 0 K and temperature T :

$$\Delta \bar{S} = \bar{S}(T) - \bar{S}(0) = \int_0^T \frac{\bar{C}_P}{T} dT = \int_0^T \frac{aT^3}{T} dT = a \int_0^T T^2 dT = \frac{a}{3} T^3 = \frac{\bar{C}_P}{3} \quad (\bar{C}_P = aT^3)$$

$$\Rightarrow \bar{S}(T) = \bar{S}(0) + \frac{\bar{C}_P}{3} \Rightarrow \bar{S}(T) = \bar{S}(0) + 0.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

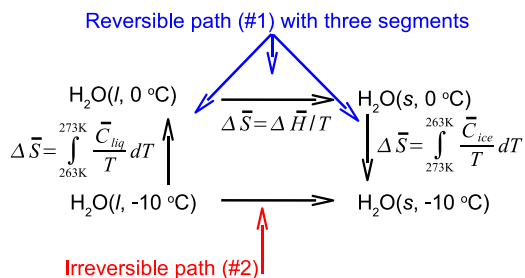
3.4 Entropy changes in irreversible processes

To obtain the change in entropy in an irreversible process we have to calculate ΔS along a reversible path between the initial state and the final state.

Example. Calculate the entropy change when supercooled water at -10°C freezes.

Solution. The process is clearly irreversible because you can not simply carry it out slowly. Any attempt to unfreeze the liquid would require, for example, an increase in temperature. This would correspond to another choice of path.

Because the process is irreversible, we have to find another path that consists of reversible segments:



$$\Delta \bar{H} = -6004 \text{ J mol}^{-1}, \bar{C}_{liq} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}, \bar{C}_{ice} = 36.8 \text{ J K}^{-1} \text{ mol}^{-1}.$$

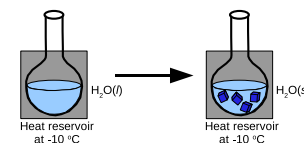
The system entropy is obtained as a sum over the three segments (the heat capacities correspond to constant-pressure values; C_P):

$$\begin{aligned} \Delta \bar{S}_{sys} &= \int_{263\text{K}}^{273\text{K}} \frac{\bar{C}_{liq}}{T} dT + \frac{\Delta \bar{H}}{T} + \int_{273\text{K}}^{263\text{K}} \frac{\bar{C}_{ice}}{T} dT = (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\times \ln\left(\frac{273\text{K}}{263\text{K}}\right) + \frac{-6004 \text{ J mol}^{-1}}{273\text{K}} + (36.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{263\text{K}}{273\text{K}}\right) \\ &= -20.54 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned} \quad (3.183)$$

According to the statistical interpretation of thermodynamics, the decrease in entropy here corresponds to increased order in ice (i.e., molecules are more rigid in the solid material than in the liquid).

Example. What is the change in entropy of the surroundings (the glass bottle plus a large heat bath at -10°C) in the previous example? What happens to the total entropy?

Solution. The process is (the gray area is the heat bath):



Because the surroundings (bottle plus bath) are large, their temperature does not change remarkably during the heat transfer from the system. Heat transfer by an infinitely small amount at constant temperature from the system to the surroundings is a reversible process (i.e. it can be done the other way around as well). Thus, for the surroundings, a reversible path is the direct path (#2 in previous diagram): $\text{H}_2\text{O} (l, -10^\circ\text{C}) \rightarrow \text{H}_2\text{O} (s, -10^\circ\text{C})$.

We use the Eq. (3.176) to calculate the change in the entropy for the surroundings:

$$\Delta\bar{S}_{surr} = \frac{q_{surr}}{T} = \frac{-q_{sys}}{T} = \frac{-\Delta\bar{H}_{263\text{ K}}}{T}$$

where we have to calculate the heat of fusion at 263 K for the system. In the previous example it was given at 273 K. To do this, we use the same idea as in the Eq. (2.140):

$$\begin{aligned}\Delta\bar{H}_{263\text{ K}} &= \int_{263\text{ K}}^{273\text{ K}} \bar{C}_{liq} dT + \Delta\bar{H}_{273\text{ K}} + \int_{273\text{ K}}^{263\text{ K}} \bar{C}_{ice} dT \\ &= \bar{C}_{liq}\Delta T + \Delta\bar{H}_{273\text{ K}} + \underbrace{-\bar{C}_{ice}\Delta T}_{\text{limits!}} = (75.3\text{ J K}^{-1}\text{mol}^{-1}) \times (10\text{ K}) \\ &\quad - 6004\text{ J mol}^{-1} - (36.8\text{ J K}^{-1}\text{mol}^{-1}) \times (10\text{ K}) = -5619\text{ J mol}^{-1}\end{aligned}$$

Now we can calculate the entropy change (Eq. (3.176)):

$$\Delta\bar{S}_{surr} = \frac{5619\text{ J mol}^{-1}}{263\text{ K}} = 21.37\text{ J K}^{-1}\text{mol}^{-1}$$

The total entropy change (system + surroundings) is the the sum of the two:

$$\begin{aligned}\Delta S_{total} &= \Delta S_{syst} + \Delta S_{surr} = (-20.54\text{ J K}^{-1}\text{mol}^{-1}) + (21.37\text{ J K}^{-1}\text{mol}^{-1}) \\ &= 0.83\text{ J K}^{-1}\text{mol}^{-1} > 0\end{aligned}$$

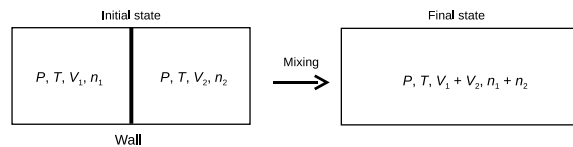
Notes:

- ▶ The total change is positive, indicating a spontaneous (irreversible) process. This is in line with Eq. (3.173).
- ▶ The non-zero ΔS arises from the differences in reversible paths (#1 and #2) for the system and the bath. For the system (water/ice) the path #1 is reversible and for the bath path #2 is reversible. Only reversible paths can be used in calculating entropies. Along path #2 the temperature is constant.

Trouton's rule: A wide range of liquids have approximately the same entropy of vaporization (*ca.* $85\text{ J K}^{-1}\text{mol}^{-1}$). This is an empirical result.

3.5 Entropy of mixing ideal gases

Consider mixing of two species of ideal gas:



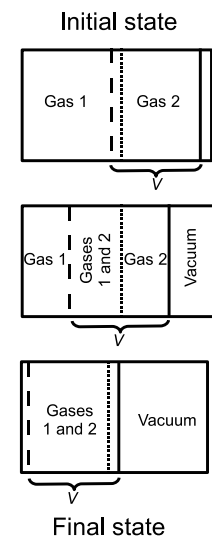
If the wall is just removed, we have clearly an irreversible process. However, in order to calculate change in entropy, we need a reversible path ($V = V_1 + V_2$):

1. Isothermal reversible expansion of each gas to the final volume V .
2. Reversible mixing of gases at constant volume V .

Segment 1 is understandable, but how can we carry out segment 2 reversibly?

Consider step 2 first (i.e. both gases have been already expanded to V):

135



Permeable membranes overlap. The non-permeable membrane is all the way to the right.

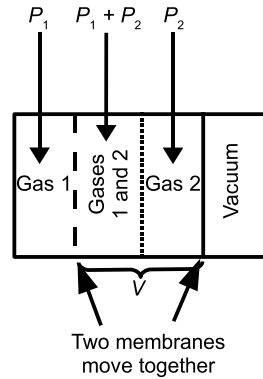
The non-permeable membrane is moved towards the left end. At the same time the “Gas 1” permeable membrane is moved towards the left end. The “Gas 2” permeable membrane is kept at the center.

The “Gas 1” permeable membrane is finally moved all the way to the left. The non-permeable membrane has been moved to the center. “Gas 2” and non-permeable membranes are on top of each other.

Dashed line	= Membrane permeable to “Gas 1”	This process is reversible. It can proceed in both directions.
Dotted line	= Membrane permeable to “Gas 2”	
Continuous line	= Non-permeable membrane	

Is there any PV -work involved in (frictionless) movement of the membranes?

No, consider the following figure:



When the two membranes move to the left, there are equal pressures on both sides: Gas 1 (P_1) + Gas 2 (P_2) and Gases 1 and 2 ($P_1 + P_2$). Both pressure and volume are constant during the process and hence no work is done: $w = 0$.

Since we are dealing with ideal gases at constant temperature, the change in internal energy (ΔU) is zero. Recall that for ideal gases the internal energy depends only on temperature (see Eq. (2.117)). Now the first law of thermodynamics ($\Delta U = q + w$) yields $q = -w = 0$ ($w = 0$ from the previous page). No changes in heat also means that there is no change in entropy and hence, for this segment, $\Delta S = 0$.

We still need to consider the first segment (step 1). Now Eq. (3.181) can be applied:

$$\text{For gas 1: } \Delta S_1 = -n_1 R \ln \left(\frac{V_1}{V} \right) = -n_1 R \ln \left(\frac{n_1}{n_1 + n_2} \right) = -n_1 R \ln(y_1) \quad (3.184)$$

$$\text{For gas 2: } \Delta S_2 = -n_2 R \ln \left(\frac{V_2}{V} \right) = -n_2 R \ln \left(\frac{n_2}{n_1 + n_2} \right) = -n_2 R \ln(y_2) \quad (3.185)$$

The total change in entropy due to mixing is given as a sum:

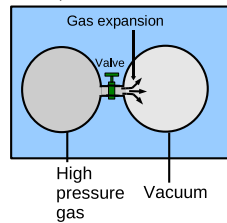
$$\Delta S_{\text{mixing}} = -n_1 R \ln(y_1) - n_2 R \ln(y_2) \quad (3.186)$$

or, in general:

$$\Delta S_{\text{mixing}} = -R \sum_{i=1}^{N_s} n_i \ln(y_i) > 0 \quad (3.187)$$

3.6 Entropy and statistical probability

Consider again Joule's experiment (both bulbs with equal volume):



With just one gas molecule, after opening the stopcock, the molecule can be in either bulb. Thus the number of equally probable arrangements is 2. With two gas molecules, they can be located both on the left, one on each side (two possibilities) and both on the right. This gives 4 equally probable arrangements. For n molecules the number of equally probable arrangements is:

# of molecules	Number of possible arrangements
2	$2^2 = 4$
3	$2^3 = 8$
4	$2^4 = 16$
...	...
n	$2^n = \exp(\ln(2^n))$

For one mole of molecules, $N = 6.022 \times 10^{23}$ ($n = 1$). The number of equally probable arrangements is:

$$2^{6.022 \times 10^{23}} = e^{4.174 \times 10^{23}} \quad (3.188)$$

Boltzmann's postulate:

$$S = k \ln(\Omega) \quad (3.189)$$

where k is Boltzmann's constant ($= R \times N_A$) and Ω is the number of equally probable microscopic arrangements for the system. The numerical value for k is $1.38066 \times 10^{-23} \text{ J K}^{-1}$. For changes in entropy the equation has the form:

$$\Delta S = S' - S = k \ln\left(\frac{\Omega'}{\Omega}\right) \quad (3.190)$$

Consider now the Joule's experiment. In the initial state all molecules are in the left bulb and there is only one possible arrangement, $\Omega = 1$. After opening the valve and reaching the equilibrium the number of possible arrangements is given by Eq. (3.188):

$$\Omega' = e^{4.174 \times 10^{23}} \text{ (final state) and } \Omega = 1 \text{ (initial state)}$$

$$\Delta S = k \ln\left(\frac{\Omega'}{\Omega}\right) = (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (4.174 \times 10^{23}) = 5.76 \text{ J K}^{-1}$$

This is positive because entropy increases when volume increases. Note that if we chose two different volumes for the bulbs, then $\Omega \propto V_1$ and $\Omega' \propto V_2$ and we would recover the $\ln\left(\frac{V_1}{V_2}\right)$ form that we found earlier.

If we compare this result with the one we calculated earlier (“expansion of ideal gas”), we note that they are identical (earlier we obtained $R \ln(2) \approx 5.76$). This gives strong support for Boltzmann’s postulate (but does not prove that it is correct).

Because of Eq. (3.169), $\Delta S \geq q/T$, the entropy is a measure of heat flow between the system and the surroundings. When heat is absorbed by the system from its surroundings, q is positive, and the entropy of the system increases. On the microscopic scale, the entropy is a measure of the dispersal of energy among the possible microstates of molecules in a system (“degrees of freedom”).

Notes:

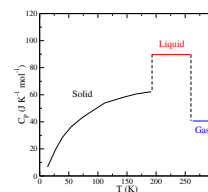
- ▶ Since thermodynamics is a statistical theory, it works only when we have a large number of atoms/molecules.
- ▶ Some processes happen spontaneously even though they do not reduce the energy of a system. They are driven purely by favorable change in entropy! From the statistical point of view, it means that states with most degrees of freedom are favored.

3.7 General expression for evaluating entropy

The entropy of a substance at any desired temperature relative to its entropy at absolute zero may be obtained by integrating dq/T from absolute zero to the desired temperature:

$$\bar{S}_T^\circ - \bar{S}_0^\circ \text{ K} = \int_{0 \text{ K}}^{T_m} \frac{\bar{C}_P^\circ(s)}{T} dT + \frac{\Delta H_{fus}^\circ}{T_m} + \int_{T_m}^{T_b} \frac{\bar{C}_P^\circ(l)}{T} dT + \frac{\Delta H_{vap}^\circ}{T_b} + \int_{T_b}^T \frac{\bar{C}_P^\circ(g)}{T} dT \quad (3.191)$$

where T_m is the melting temperature and T_b is the boiling temperature. If temperature T is smaller than T_m or T_b , the corresponding terms are omitted. The enthalpies have the following notation: *fus* (fusion; crystallization/melting) and *vap* (vaporization). Note that all the heat capacities in this expression depend on temperature:



Heat capacity of sulfur dioxide at a constant pressure of 1 bar.

Entropy of sulfur dioxide at different temperatures ($T_m = 197.64$ K, $T_b = 263.08$ K, $\Delta\bar{H}_{fus} = 7402$ J mol⁻¹, $\Delta\bar{H}_{vap} = 24937$ J mol⁻¹):

T (K)	Method of calculation	$\Delta\bar{S}^\circ$ (J K ⁻¹ mol ⁻¹)
0 – 15	Debye function ($\bar{C}_P \propto T^3$)	1.26
15 – 197.64	Graphical, solid	84.18
197.64	Fusion, $\Delta\bar{H}_{fus}/T_m$	37.45
197.64 – 263.08	Graphical, liquid	24.94
263.08	Vaporization, $\Delta\bar{H}_{vap}/T_b$	94.79
263.08 – 298.15	From \bar{C}_P of gas	5.23
$\bar{S}^\circ(298.15 \text{ K}) - \bar{S}^\circ(0 \text{ K}) =$		247.85

3.8 Third law of thermodynamics

The third law, for all molecules:

$$\lim_{T \rightarrow 0} \Delta_r S = 0 \quad (3.192)$$

Planck's contribution, for any pure substance:

$$\lim_{T \rightarrow 0} S = 0 \quad (3.193)$$

Consider a simple phase change in Eq. (3.192):

Sulfur(rhombic crystal) \leftrightarrow Sulfur(monoclinic cry:

Experimental determination of heat capacities and Eq. (3.191) show that:

$$\Delta_r S \rightarrow 0$$

On the right: experimentally determined entropies for the two crystal forms of sulfur are shown.



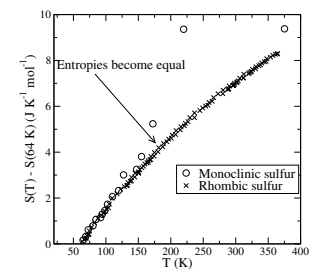
Walther Nernst,
German chemist
(1864 - 1941)



Theodore W. Richards,
American chemist
(1868 - 1928)



Max Planck,
German physicist
(1858 - 1947)



Experimental details for the phase change in solid sulfur:

- ▶ Rhombic form of sulfur is the stable form below the phase transition temperature (368.5 K).
- ▶ Monoclinic sulfur can exist below this temperature when supercooled.

Experimental methods for determining $\Delta_r S$:

Method 1: Determine constant-pressure heat capacities ($C_P(T)$) for both forms of the crystal structures. Use Eq. (3.191):

$$\begin{aligned}\bar{S}_{368.5 \text{ K}}^{\text{rho}} - \bar{S}_{0 \text{ K}}^{\text{rho}} &= \int_{0 \text{ K}}^{368.5 \text{ K}} \frac{\bar{C}_P^{\text{rho}}}{T} dT \\ \bar{S}_{368.5 \text{ K}}^{\text{mon}} - \bar{S}_{0 \text{ K}}^{\text{mon}} &= \int_{0 \text{ K}}^{368.5 \text{ K}} \frac{\bar{C}_P^{\text{mon}}}{T} dT\end{aligned}\quad (3.194)$$

If we assume that both rhombic and monoclinic forms have the same $S_{0 \text{ K}}$ then subtraction of the equations from each other gives the entropy difference between the two forms at 368.5 K. The result from such calculation gives $\Delta S(\text{rho}, \text{mon})$ at 368.5 K, which is $1.09 \text{ J K}^{-1} \text{ mol}^{-1}$.

Method 2: Determine heats of combustion for both crystal forms at 368.5 K and calculate the enthalpy difference between the two forms by subtracting the two values from each other. Then use Eq. (3.176):

$$\Delta S(\text{rho}, \text{mon}) = \frac{\Delta H}{T} = \frac{401 \text{ J mol}^{-1}}{368.5 \text{ K}} = 1.09 \text{ J K}^{-1} \text{ mol}^{-1} \quad (3.195)$$

Both methods give consistent results. Note that we used the fact that both species had identical entropies at 0 K. Statistical thermodynamics says that this value should be zero.

Notes:

1. What is supercooling? A liquid below its melting point will crystallize in presence of a seed crystal or nucleus around which a crystal structure can form. However, lacking any such nucleus, the liquid phase can be maintained all the way down to the temperature at which crystal homogeneous nucleation occurs. For example, pure water can be cooled to almost 231 K (melting point 273 K) when cooled very fast, about at rate 1 million K / second. Rain contains sometimes supercooled water, which freezes immediately upon touching a surface.
2. C_P goes to zero when temperature approaches 0 K.
3. According to the third law of thermodynamics, it is impossible to reach 0 K.

Other methods for determining entropy:

- ▶ Measurement of equilibrium constant for a chemical reaction over a range of temperatures yields both ΔH° and ΔS° .
- ▶ Spectrophotometric measurements

Violations of the third law?

In most cases theory and experiment agree (298.15 K and 1 bar; gas):

Gas	S° (Calc.) / J K ⁻¹ mol ⁻¹	S° (Exp.) / J K ⁻¹ mol ⁻¹
CO ₂	213.8	213.7
NH ₃	192.8	192.6
NO ₂	240.1	240.2
CH ₄	186.3	186.3
C ₂ H ₂	200.9	200.9
C ₂ H ₄	219.6	219.6
C ₂ H ₆	229.6	229.6
N ₂ O	215.1	219.9 ($\Delta = 4.8$)
CO	193.5	197.7 ($\Delta = 4.2$)

This suggests that there is some kind of residual entropy in the system? When comparing values obtained using heat capacities and spectroscopic data, similar discrepancies can be noticed.

For both CO and N₂O, the residual entropy can be explained by imperfect crystal structures at 0 K, which results in approximately a constant offset at elevated temperatures as well (see previous table). Crystal imperfections contribute to the total entropy and hence it does not approach zero even at 0 K. Consider the following molecular arrangements in solid N₂O:



In other words, the molecule can orient in many different ways in the crystal (O \dots O, O \dots N, N \dots N). If we consider that N₂O gas would consist of two different species NNO and ONN with equal amounts and calculate the entropy of mixing these two species, we get (Eq. (3.186) for per mole quantity, $y_1 = 1/2, y_2 = 1/2$):

$$\begin{aligned} \Delta_{mix} \bar{S} &= -n_1 R \ln(y_1) - n_2 R \ln(y_2) = -\frac{1}{2} R \ln\left(\frac{1}{2}\right) - \frac{1}{2} R \ln\left(\frac{1}{2}\right) \quad (3.196) \\ &= 5.8 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

This is approximately the difference between the experimental and calculated results. If we could prepare a “perfect” crystal somehow, this correction would not be needed. For CO, one needs to consider two “different” molecules CO and OC.

The following two sources of randomness in crystals at 0 K are not considered in calculating the entropies for chemical purposes:

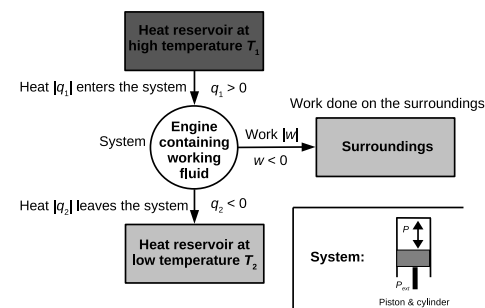
1. Possible isotopic mixtures of species. This is ignored because both the reactants and the products contain the same mixture isotopes.
2. Spin degeneracy at 0 K is ignored. Again the same degeneracy exists in both the reactants and the products. Spin is conserved in chemical reactions.

Notes:

1. The entropy of H^+ (at chemical equilibrium) in water has been arbitrarily assigned the value of zero.
2. When comparing standard entropy values from various sources, it is important to be aware of the standard pressure used.
3. In order to see why NNO vs. ONN (or CO vs. OC) configurations result in residual entropy, one should draw the crystal structure and look at the possible orientations there.
4. H_2O is another system that has significant amount of residual entropy.

3.9 Heat engines

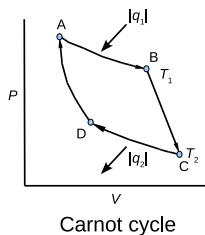
Heat engine is an engine that uses heat to generate mechanical work:



Carnot heat engine:

1. Isothermal expansion
2. Adiabatic expansion
3. Isothermal compression
4. Adiabatic compression

Consider the $P - V$ plot of the Carnot heat engine (the four cycles are denoted by A, B, C, D, all processes are reversible):



1. **A → B:**
 - ▶ Heat q_1 is transferred from the high-temperature (isothermal at temperature T_1) reservoir to the cylinder
 - ▶ Isothermal expansion of the gas pushes the piston towards larger cylinder volume
 - ▶ The moving piston does work on the surroundings (w_1)
 - ▶ $\Delta U_1 = q_1 + w_1$
2. **B → C:**
 - ▶ Adiabatic expansion of the gas
 - ▶ The expansion continues until temperature of the gas drops from T_1 to T_2
 - ▶ During this stage the piston does work on the surroundings (w_2)
 - ▶ $\Delta U_2 = w_2$
3. **C → D:**
 - ▶ Isothermal compression of the gas
 - ▶ The surroundings does work on the piston (w_3)
 - ▶ Heat flows out to the low-temperature reservoir (q_2)
 - ▶ $\Delta U_3 = q_2 + w_3$
4. **D → A:**
 - ▶ Adiabatic compression of the gas
 - ▶ The surroundings do work on the piston (w_4)
 - ▶ No heat exchange
 - ▶ A steam engine with two stages
 - ▶ $\Delta U_4 = w_4$

Because the internal energy of the system is a state function, the total change in internal energy over a closed path must be zero:

$$\Delta U_{cycle} = \underbrace{\left(\overbrace{q_1}^{q_{in}} + \overbrace{q_2}^{q_{out}} \right)}_{\equiv q_{cycle}} + \underbrace{(w_1 + w_2 + w_3 + w_4)}_{\equiv w_{cycle}} \quad (3.197)$$

$$\Rightarrow -w_{cycle} = q_{cycle} = q_{in} + q_{out} \quad (3.198)$$

$$\Rightarrow |w_{cycle}| = |q_{in}| - |q_{out}| \quad (q_{in} > 0 \text{ and } q_{out} < 0) \quad (3.199)$$

In order to find out the efficiency of the heat engine, we define the efficiency parameter ϵ :

$$\epsilon = \frac{|w_{cycle}|}{|q_{in}|} = \frac{|q_{in}| - |q_{out}|}{|q_{in}|} = 1 - \frac{|q_{out}|}{|q_{in}|} \quad (3.200)$$

Note that $0 < \epsilon < 1$ and larger value of ϵ correspond to better efficiency.

Next we apply the concept of entropy to simplify Eq. (3.200). Because the overall cycle is reversible, the total entropy change over the closed cycle is zero. Only two segments along the path deal with heat exchange (**A-B** and **C-D**). For these segments Eq. (3.166) gives (T_{in} and T_{out} correspond to T_1 and T_2 , respectively):

$$\Delta S_{cycle} = \frac{|q_{in}|}{T_h} - \frac{|q_{out}|}{T_c} = 0 \Rightarrow \frac{|q_{in}|}{T_h} = \frac{|q_{out}|}{T_c} \quad (3.201)$$

$$\epsilon = 1 - \frac{T_c}{T_h} \quad (3.202)$$

Thus the ratio of T_c/T_h must be made as small as possible to achieve high efficiency. Typically T_c would be room temperature, and therefore T_h should simply be made as high as possible.

*“Legendre transformation allows definition of useful thermodynamic potentials:
Helmholtz and Gibbs potentials”*

4.1 Fundamental equation for the internal energy

155

Let's first recall what we have learned so far:

The first law of thermodynamics (Eq. (2.64)): $dU = dq + dw$

The second law of thermodynamics (Eq. (3.169)): $dS \geq \frac{dq}{T}$

Consider a closed system with only reversible PV -work: $dw = -PdV$ and $dS = \frac{dq}{T}$

Combining this with the 1st and 2nd laws gives: $dU = TdS - PdV$.

When chemical potential is included above, we get the generalized form for dU :

$$dU = TdS - PdV + \underbrace{\sum_{i=1}^{N_s} \mu_i dn_i}_{\text{"chemical work"}} \quad (4.203)$$

where N_s is the number of chemical species, μ_i is the chemical potential and n_i is the amount of substance of species i .



J. Willard Gibbs,
American physicist
(1839 - 1903)

Note that U depends on variables S, V and $\{n_i\}$. These variables are called the *natural variables* of U . The total differential of U can be written as (cf. Eq. (1.45)):

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, \{n_i\}} dS + \left(\frac{\partial U}{\partial V} \right)_{S, \{n_i\}} dV + \sum_{i=1}^{N_s} \left(\frac{\partial U}{\partial n_i} \right)_{S, V, \{n_j\}_{j \neq i}} dn_i \quad (4.204)$$

If this is compared with Eq. (4.203), we can see that partial derivatives in front of dS , dV and dn_i must be equal to T , $-P$ and μ_i , respectively:

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, \{n_i\}}, P = - \left(\frac{\partial U}{\partial V} \right)_{S, \{n_i\}}, \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, \{n_j\}_{j \neq i}} \quad (4.205)$$

Thus if we know the partial derivatives of the internal energy with respect to S , V and n_i , we can calculate T , P and μ_i using Eq. (4.205).

If we allow the process to be irreversible, we have to consider the inequality in the second law and keep in mind that the pressure now is really P_{ext} :

$$dU \leq TdS - P_{ext}dV + \sum_{i=1}^{N_s} \mu_i dn_i \quad (4.206)$$

If the entropy, volume and amounts of substance are constant, we have:

$$(dU)_{S,V,\{n_i\}} \leq 0 \quad (4.207)$$

This is the criterion for spontaneous change and equilibrium at constant S , V and n_i . At equilibrium, $U(S, V, \{n_i\})$ must be at minimum (i.e., $dU = 0$).

If T , P , and μ_i are constant, Eq. (4.203) can be integrated:

$$U = TS - PV + \sum_{i=1}^{N_s} \mu_i n_i \quad (4.208)$$

Note: It is not convenient to use S and V as variables because they cannot be easily controlled during chemical processes.

4.2 Definitions of additional thermodynamic potentials using Legendre transformations

What is Legendre transformation? Consider the following differential:

$$df(x, y) = \left(\frac{\partial f(x, y)}{\partial x} \right) dx + \left(\frac{\partial f(x, y)}{\partial y} \right) dy \equiv u(x, y)dx + v(x, y)dy$$

Change the differentials from (dx, dy) to (du, dy) with the following transformation:

$$g \equiv f - ux$$

$$dg = df - udx - xdu = udx + vdy - udx - xdu = vdy - xdu$$

where $x = -\frac{\partial g}{\partial u}$ and $v = \frac{\partial g}{\partial y}$. x and u are *conjugate variables*.

In a nutshell:

“Transform the original differential in such a way that the new differential depends on the conjugate variables”



Adrien-Marie Legendre,
French mathematician
(1752 - 1833)

Next, we will apply Legendre transformation to internal energy (ignore chemical potential for now):

$$\underbrace{dU}_{\text{"f"}} = \underbrace{-P}_{\text{"u"}} \underbrace{dV}_{\text{"dx"}} + \underbrace{T}_{\text{"v"}} \underbrace{dS}_{\text{"dy"}}$$

$$\underbrace{H}_{\text{"g"}} = \underbrace{U}_{\text{"f"}} - \underbrace{(-PV)}_{\text{"u \times x"}} = U + PV$$

$$\underbrace{dH}_{\text{"dg"}} = \underbrace{T}_{\text{"v"}} \underbrace{dS}_{\text{"dy"}} - \left(\underbrace{V}_{\text{"x"}} \times \underbrace{(-dP)}_{\text{"du"}} \right) = TdS + VdP$$

Now we have a new differential (enthalpy) dH with new natural variables S and P . Note that the original differential dU had S and V as natural variables. Adding chemical potential does not change this result since we were not operating on the corresponding conjugate variables (μ_i and n_i):

$$dH = TdS + VdP + \sum_{i=1}^{N_s} \mu_i dn_i \quad (4.209)$$

Recall that the total differential of H is:

$$dH = \left(\frac{\partial H}{\partial S} \right)_{P, \{n_i\}} dS + \left(\frac{\partial H}{\partial P} \right)_{S, \{n_i\}} dP + \sum_{i=1}^{N_s} \left(\frac{\partial H}{\partial n_i} \right)_{P, V, \{n_j\}_{j \neq i}} dn_i \quad (4.210)$$

By comparing the terms the same way as we did for dU , we get the following relations:

$$T = \left(\frac{\partial H}{\partial S} \right)_{P, \{n_i\}}, V = \left(\frac{\partial H}{\partial P} \right)_{S, \{n_i\}}, \mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S, P, \{n_j\}_{j \neq i}} \quad (4.211)$$

Thus, if we can determine the partial derivatives of H with respect to S , P and n_i , we can always obtain T , V and μ_i from Eq. (4.211). A system under constant S , P , and n_i combined with Eq. (4.209) and exactly the same reasoning as in Eq. (4.207) gives:

$$(dH)_{S, P, \{n_i\}} \leq 0 \quad (4.212)$$

A process occurs spontaneously at constant S , P and $\{n_i\}$ if the enthalpy decreases.

Furthermore, integration of Eq. (4.209) under constant T , P and $\{\mu_i\}$ results in:

$$H = TS + \sum_{i=1}^{N_s} \mu_i n_i \quad (4.213)$$

Note that this yields Eq. (4.208) when setting $H = U + PV$.

161

Previously we established that U and H are connected to each other via Legendre transformation with conjugate variables V and P . It is easier to control pressure than volume and therefore H is more convenient to use in practice.

How about the other conjugate variable pair (T, S) ?

Yes, it is more convenient to use temperature rather than entropy. Since (V, P) pair offers two choices (U and H) and (T, S) another two, we have a total of four different possibilities:

Quantity	Natural variables	Energy	Differential (*)
Internal energy U	$S, V, \{n_i\}$	U	$dU = TdS - PdV$
Enthalpy H	$S, P, \{n_i\}$	$H = U + PV$	$dH = TdS + VdP$
Helmholtz energy A	$T, V, \{n_i\}$	$A = U - TS$	$dA = -SdT - PdV$
Gibbs energy G	$T, P, \{n_i\}$	$G = H - TS$	$dG = -SdT + VdP$

(*) chemical potential should be added to each differential. We are not considering Legendre transformation with respect to n_i and μ_i . The differential can also be derived from the given energy expression by considering the total differential.

The last form is most useful in chemical applications since T and P can be controlled (i.e. they can be held constant).

Expressions for the Helmholtz “free energy” (A):

$$dA = -SdT - PdV + \sum_{i=1}^{N_s} \mu_i dn_i \quad (4.214)$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V, \{n_i\}} \quad (4.215)$$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, \{n_i\}} \quad (4.216)$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, \{n_j\}_{j \neq i}} \quad (4.217)$$

$$(dA)_{T, V, \{n_j\}_{j \neq i}} \leq 0 \quad (4.218)$$

$$A = -PV + \sum_{i=1}^{N_s} \mu_i n_i \quad (4.219)$$



Hermann von Helmholtz,
German physicist (1821 -
1894)

At constant T , a change in the Helmholtz energy is given by $\Delta A = \Delta U - T\Delta S$. This gives the amount of internal energy that is “free” for doing work in a spontaneous process.

Note: Helmholtz energy is less useful in chemistry than the Gibbs energy because processes and reactions are more often carried out at constant pressure rather than constant volume.

The corresponding expressions for the Gibbs energy (G) are:

$$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i \quad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,\{n_i\}} \quad (4.223)$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P,\{n_i\}} \quad (dG)_{T,P,\{n_i\}} \leq 0 \quad (4.224)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,\{n_i\}} \quad G = \sum_{i=1}^{N_s} \mu_i n_i (\text{const. } T, P, \mu_i) \quad (4.225)$$

At constant T and P , a change in the Gibbs energy is given by: $\Delta G = \Delta U + P\Delta V - T\Delta S$. In another words, it gives the maximum amount of internal energy that is available for doing non-expansion work in a spontaneous process.

The related Maxwell equations (differentiation of the previous Eqs.):

$$\left(\frac{\partial S}{\partial P} \right)_{T,\{n_i\}} = - \left(\frac{\partial^2 G}{\partial P \partial T} \right)_{T,\{n_i\}} = - \left(\frac{\partial^2 G}{\partial T \partial P} \right)_{P,\{n_i\}} = - \left(\frac{\partial V}{\partial T} \right)_{P,\{n_i\}} \quad (4.226)$$

$$\left(\frac{\partial S}{\partial n_i} \right)_{P,T,\{n_j\}_{j \neq i}} = - \left(\frac{\partial^2 G}{\partial n_i \partial T} \right)_{P,T,\{n_j\}_{j \neq i}} = - \left(\frac{\partial^2 G}{\partial T \partial n_i} \right)_{P,\{n_i\}} = - \left(\frac{\partial \mu_i}{\partial T} \right)_{P,\{n_i\}} \quad (4.227)$$

$$\left(\frac{\partial V}{\partial n_i} \right)_{P,T,\{n_j\}_{j \neq i}} = \left(\frac{\partial^2 G}{\partial n_i \partial P} \right)_{P,T,\{n_j\}_{j \neq i}} = \left(\frac{\partial^2 G}{\partial P \partial n_i} \right)_{T,\{n_i\}} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,\{n_i\}} \quad (4.228)$$

Note: Since G is a well behaving, the order of differentiation may changed.

Example. Demonstrate the fact that if a thermodynamic potential is known as a function of its natural variables, we can calculate all of the thermodynamic properties of the system.

Solution. We choose to show this for the Gibbs energy (G). So we assume that the value of G is known as a function of its natural variables ($T, P, \{n_i\}$). In this example we will consider only single species, so that the chemical potential sum vanishes. The entropy and volume of the system can be calculated using (Eqs. (4.221) and (4.222)):

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P} \right)_T$$

Now using the equations given in the previous table, we have:

$$U = G - PV + TS = G - P \left(\frac{\partial G}{\partial P} \right)_T - T \left(\frac{\partial G}{\partial T} \right)_P$$

$$H = G + TS = G - T \left(\frac{\partial G}{\partial T} \right)_P \quad \text{and} \quad A = G - PV = G - P \left(\frac{\partial G}{\partial P} \right)_T$$

These expressions relate U , H , A , and G to each other.

Example. Show that the Gibbs energy gives a criterion for spontaneous change at constant $T = T_{sys} = T_{surr}$ and P .

Solution. We need to show that $dG_{sys} \leq 0 \Leftrightarrow dS_{tot} \geq 0$. First we calculate dG_{sys} by noting that $G = H - TS$:

$$\begin{aligned} dG_{sys} &= d(H_{sys} - TS_{sys}) = dH_{sys} - d(TS_{sys}) = dH_{sys} - \underbrace{S_{sys}dT}_{=0} - TdS_{sys} \\ &= dq_{sys} - TdS_{sys} = -dq_{surr} - TdS_{sys} \leq 0 \\ &\Leftrightarrow \underbrace{\frac{dq_{surr}}{T}}_{=dS_{surr}} + dS_{sys} = dS_{tot} \geq 0 \end{aligned}$$

Thus for spontaneous (irreversible) changes, the Gibbs energy will always decrease with the equal sign applying only to reversible processes. Note that there is no need to consider the surroundings explicitly when predicting spontaneity using Gibbs energy whereas the calculation using entropy must consider both the system and surroundings explicitly.

Note: Although the above criteria show whether a certain change is spontaneous, it does not necessarily follow that the change will take place with an appreciable speed.

When other than PV -work occurs in the system, it contributes a term to the fundamental equation for the internal energy (Eq. (2.95)). They can be included in the Gibbs energy:

$$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i + FdL + \gamma dA_S \quad (4.229)$$

where F is the force of extension, L is the length, γ is the surface tension and A_S is the surface area. Variables (F and L) and (γ and A_S) are conjugate variables and:

$$F = - \left(\frac{\partial G}{\partial L} \right)_{T,P,\{n_i\},A_S} \quad (4.230)$$

$$\gamma = \left(\frac{\partial G}{\partial A_S} \right)_{T,P,\{n_i\},L} \quad (4.231)$$

What is the meaning of the Helmholtz and Gibbs energies in presence of non- PV work?

1. *Helmholtz energy.* Consider the first law of thermodynamics (Eq. (2.64)): $dU = dq + dw$. Using Eq. (3.172) gives:

$$-dU + TdS \geq -dw \quad (4.232)$$

At constant temperature ($dT = 0$) we can write:

$$-d(U - TS) \geq -dw \quad (4.233)$$

This implies that:

$$(dA)_T \leq d\mathfrak{w} \quad (4.234)$$

where A is the Helmholtz energy. Thus a change in the Helmholtz energy gives an upper bound for the work that can be done on the surroundings. In real processes the *amount* work that can be done is less than $|\Delta A|$. In this case both sides of Eq. (4.234) are negative ($d\mathfrak{w} < 0$ and $(dA)_T < 0$); i.e. when the system does work on the surroundings (i.e. $|(dA)_T| \geq |d\mathfrak{w}|$).

Note: $d\mathfrak{w}$ now contains both PV and non- PV work.

2. *Gibbs energy.* The Gibbs energy is especially useful when non- PV work is involved. When PV and non- PV work are separated, the first law of thermodynamics (Eq. (2.64)) can be written:

$$dU = d\mathfrak{q} - P_{ext}dV + d\mathfrak{w}_{nonPV} \quad (4.235)$$

With the inequality (Eq. (3.172)) $TdS \geq d\mathfrak{q}$ we can write:

$$-dU - P_{ext}dV + TdS \geq -d\mathfrak{w}_{nonPV} \quad (4.236)$$

At constant T and P ($= P_{ext}$), we have:

$$-d(U + PV - TS) \geq -d\mathfrak{w}_{nonPV} \quad (4.237)$$

$$(dG)_{T,P} \leq d\mathfrak{w}_{nonPV} \quad (4.238)$$

Notes:

1. For a reversible process at constant T and P the change in Gibbs energy is equal to the non- PV work done on the system by the surroundings.
2. Eq. (4.238) states that a change in the Gibbs energy at constant T and P gives an upper bound for the non- PV work that the system can do on its surroundings. *Remember that in this case dG and $d\mathfrak{w}_{nonPV}$ are negative.*
3. When work is done on the system, the Gibbs energy increases. When work is done by the system, the Gibbs energy decreases.

4.3 Effect of temperature on the Gibbs energy

How does G change as a function of temperature? Eq. (4.221) states that:

$$\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} = -S \leq 0$$

Since the derivative is zero or negative, the Gibbs energy decreases as T increases given that P and $\{n_i\}$ are constant.

What is the relationship between H and G in terms of temperature?

Previously we have established that $G = H - TS$. If we replace S with the above derivative:

$$G = H - TS = H + T \left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} \quad (4.239)$$

This equation can be modified by using the following expression (G on the right hand side):

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,\{n_i\}} = -\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} \quad (4.240)$$

Substitution of Eq. (4.239) into this equation gives (“the Gibbs-Helmholtz equation”):

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T}\right)_{P,\{n_i\}} \quad (4.241)$$

When looking at differences in the Gibbs energies and enthalpies, this becomes:

$$\Delta H = -T^2 \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P,\{n_i\}} \quad (4.242)$$

Notes:

1. If ΔG can be determined as a function of temperature, we can obtain ΔH using Eq. (4.242).
2. If ΔH is independent of temperature and ΔG is known at one temperature, it is possible to obtain ΔG at other temperatures with Eq. (4.242).

4.4 Effect of pressure on the Gibbs energy

How does G change as a function of pressure?

First Recall Eq. (4.222): $\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = V$.

Integration of this equation gives:

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dP \Rightarrow G_2 = G_1 + \int_{P_1}^{P_2} \underbrace{V}_{>0} dP \quad (4.243)$$

Thus *the Gibbs energy always increases with the increasing pressure* when T and $\{n_i\}$ are constant.

For liquids and solids volume (V) is approx. independent of pressure (P) and thus:

$$G_2 = G_1 + V(P_2 - P_1) \text{ or } \Delta G = V\Delta P \quad (4.244)$$

For ideal gases ($PV = nRT$), we can write:

$$G_2 = G_1 + nRT \ln\left(\frac{P_2}{P_1}\right) \text{ or } \Delta G = nRT \ln\left(\frac{P_2}{P_1}\right) \quad (4.245)$$

Setting $P_2 = P, P_1 = P^\circ, G_2 = G$ and $G_1 = G^\circ$, we get:

$$G = G^\circ + nRT \ln\left(\frac{P}{P^\circ}\right) \quad (4.246)$$

Example. Given the expression for the molar Gibbs energy (Eq. (4.246)) and considering a monatomic ideal gas, derive the corresponding expression for the following thermodynamic properties: V, U, H, S and A at constant T .

Solution. The molar Gibbs energy is given by Eq. (4.246) with over bars:

$$\bar{G} = \bar{G}^\circ + RT \ln\left(\frac{P}{P^\circ}\right)$$

We need to find a similar -type expression for the above thermodynamic properties. The form should be: $X = X^\circ + \text{"possible pressure correction"}$. For an ideal gas we have:

$$P\bar{V} = RT \Rightarrow \bar{V} = \frac{RT}{P}$$

Based on Eq. (2.117), the internal energy of an ideal gas does not depend on volume or pressure but only on temperature:

$$\bar{U} = \bar{U}^\circ$$

Recall that enthalpy is defined as $H = U + PV$. For an ideal gas $PV = \text{constant} = nRT$, thus:

$$\bar{H} = \bar{U} + P\bar{V} = \bar{U}^\circ + RT = \bar{H}^\circ$$

Eq. (3.182) for the molar entropy states that: $\bar{S} = \bar{S}^\circ - R \ln \left(\frac{P}{P^\circ} \right)$.

For the Helmholtz energy we have:

$$\begin{aligned}\bar{A}^\circ &= \bar{G}^\circ - P\bar{V} = \bar{G}^\circ - RT \\ \Rightarrow \bar{A} &= \bar{G} - P\bar{V} = \bar{G} - RT = \underbrace{\bar{G}^\circ - RT}_{=\bar{A}^\circ} + RT \ln \left(\frac{P}{P^\circ} \right) = \bar{A}^\circ + RT \ln \left(\frac{P}{P^\circ} \right)\end{aligned}$$

Example. An ideal gas at 27 °C expands isothermally and reversibly from 10.00 to 1.000 bar against a pressure that is gradually reduced. Calculate q per mole and w per mole and each of the thermodynamic quantities $\Delta\bar{G}$, $\Delta\bar{U}$, $\Delta\bar{H}$, $\Delta\bar{S}$ and $\Delta\bar{A}$.

Solution. Since the process is reversible & isothermal and the gas is ideal, we have:

$$\begin{aligned}dw &= -P_{ext}d\bar{V} = -Pd\bar{V} \Rightarrow w = -RT \ln \left(\frac{\bar{V}_2}{\bar{V}_1} \right) = -RT \ln \left(\frac{P_1}{P_2} \right) \\ &= - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300.15 \text{ K}) \times \ln \left(\frac{10.00 \text{ bar}}{1.000 \text{ bar}} \right) = -5746 \text{ J mol}^{-1}\end{aligned}$$

Recall that Helmholtz energy gives the maximum amount of work that the system can do in a reversible process. Here the work and Helmholtz energy should be equal. Formally this can be seen integrating Eq. (4.214) at constant T :

$$dA = -S \underbrace{dT}_{\equiv 0} - PdV = -PdV = dw \Rightarrow \Delta\bar{A} = w = -5746 \text{ J mol}^{-1}$$

The internal energy of an ideal gas depends only on temperature and hence:

$$\Delta\bar{U} = 0 \Rightarrow q = \Delta\bar{U} - w = 5746 \text{ J mol}^{-1}$$

Likewise, the enthalpy of an ideal gas depends only on temperature:

$$\Delta\bar{H} = \Delta\bar{U} + \Delta(P\bar{V}) = \underbrace{\Delta\bar{U}}_{\equiv 0} + \underbrace{\Delta(RT)}_{\equiv 0} = 0$$

To get the change in the Gibbs energy ($\Delta\bar{G}$), we integrate Eq. (4.222):

$$\begin{aligned}\Delta\bar{G} &= \int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \bar{V} dP = \int_{P_1}^{P_2} \frac{RT}{P} dP = RT \ln \left(\frac{P_2}{P_1} \right) \\ &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300.15 \text{ K}) \times \ln \left(\frac{1.000 \text{ bar}}{10.00 \text{ bar}} \right) = -5746 \text{ J mol}^{-1}\end{aligned}$$

Entropy for a reversible process at constant T can be calculated using Eq. (3.166):

$$\Delta \bar{S} = \frac{q_{rev}}{T} = \frac{5746 \text{ J mol}^{-1}}{300.15 \text{ K}} = 19.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

Another way to calculate the entropy difference is (" $G = H - TS$ "):

$$\Delta \bar{S} = \frac{\Delta \bar{H} - \Delta \bar{G}}{T} = 19.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example. An ideal gas expands isothermally at 27 °C into an evacuated vessel so that the pressure drops from 10.00 to 1.000 bar; that is, it expands from a vessel of 2.463 L into a connecting vessel such that the total volume becomes 24.63 L. Calculate the change in thermodynamic quantities that were calculated in the previous example.

Solution. This process is isothermal but NOT reversible. Since the system as a whole is closed, no external work is done and $w = 0$. Also at constant T , $\Delta U = 0$ and hence the first law of thermodynamics implies that also $q = 0$. The other quantities are the same as in the previous example, because the quantities are state functions and the choice of path does not affect the result. Both initial and final states in this example are identical to those in the previous example.

Example. Calculate the Gibbs energy of formation at 10.00 bar and 298.15 K for: (a) Gaseous methanol (CH_3OH) (the standard Gibbs energy of formation $-161.96 \text{ kJ mol}^{-1}$) and (b) Liquid methanol (density 0.7914 g cm^{-3} and the standard Gibbs energy of formation $-166.27 \text{ kJ mol}^{-1}$). Assume that gaseous methanol behaves according to the ideal gas law.

Solution. The Gibbs energy of formation is defined essentially the same way as we defined the enthalpy of formation previously. For (a) we can use Eq. (4.246):

$$\begin{aligned} \Delta_f G &= \Delta_f G^\circ + RT \ln \left(\frac{P}{P^\circ} \right) = -161.96 \text{ kJ mol}^{-1} + (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &\quad \times (298.15 \text{ K}) \times \ln \left(\frac{10.00 \text{ bar}}{1.000 \text{ bar}} \right) = -156.25 \text{ kJ mol}^{-1} \end{aligned}$$

Thus we see that the Gibbs energy of formation is higher at higher pressure. In practice this means that it was not as favorable to form methanol at high pressure than at the low pressure. In both cases the reaction is spontaneous.

For (b) the molar volume of the liquid is approximately independent of pressure. In this case we can use directly Eq. (4.244). First we have to calculate the molar volume:

$$\bar{V} = \frac{M_{\text{CH}_3\text{OH}}}{\rho_{\text{CH}_3\text{OH}}} = \frac{32.04 \text{ g mol}^{-1}}{0.7914 \text{ g cm}^{-3}} = 40.49 \text{ cm}^3 \text{ mol}^{-1}$$

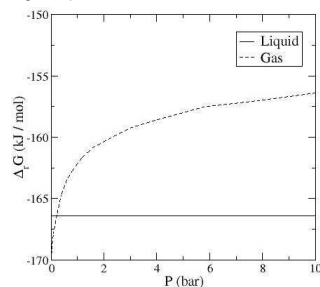
$$= (40.49 \text{ cm}^3 \text{ mol}^{-1}) \times (10^{-2} \text{ m cm}^{-1})^3 = 40.49 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

This gives the molar Gibbs energy of formation:

$$\Delta_f G = \Delta_f G^\circ + \bar{V} (P - P^\circ) = (-166.27 \text{ kJ mol}^{-1}) + (40.49 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})$$

$$\times \left(\frac{9 \times 10^5 \text{ Pa}}{10^3 \text{ J / kJ}} \right) = -166.23 \text{ kJ mol}^{-1}$$

Note: The Gibbs energy of formation for a gases and liquids have very different pressure dependency. This can be seen in the graph shown on the right (the value of the $\bar{V} \times \Delta P$ term above for the liquid is small compared to $\Delta_f G^\circ$). At the intersection, both species have the same molar volume.



4.5 Fugacity and activity

Idea: Keep the basic form of the equations that were derived for ideal gases, but use an effective pressure (“fugacity”) and effective chemical potential (“activity”).

Fugacity $f = f(P)$ would deviate from the real pressure P at high pressures. At low pressures it approaches the real pressure:

$$\lim_{P \rightarrow 0} \frac{f(P)}{P} = 1 \quad (4.247)$$

For example, the Gibbs energy (Eq. (4.246)) in terms of fugacity is:

$$\bar{G} = \bar{G}^\circ + RT \ln \left(\frac{f}{P^\circ} \right) \quad (4.248)$$

Note that fugacity has the units of pressure. Also, for a real gas, it is directly related to the Gibbs energy. If the equation of state for a real gas is known, it is possible to calculate the fugacity.



Gilbert Newton Lewis, American physical chemist (1875 - 1946)

Derivation of expression for fugacity for a real gas at constant temperature:

First recall Eq. (4.222): $V = \left(\frac{\partial G}{\partial P} \right)_{T, \{n_i\}}$

At constant temperature: $d\bar{G} = \bar{V}dP$ (real gas) and $d\bar{G}^{id} = \bar{V}^{id}dP$ (ideal gas)

The Gibbs energy differential between the real and ideal gases is:

$$d(\bar{G} - \bar{G}^{id}) = (\bar{V} - \bar{V}^{id})dP$$

Integration of both sides gives:

$$\int_{G(P^*)}^{G(P)} d(\bar{G} - \bar{G}^{id}) = \int_{P^*}^P (\bar{V} - \bar{V}^{id})dP \quad (4.249)$$

Performing the integration yields:

$$(\bar{G} - \bar{G}^{id})_P - (\bar{G} - \bar{G}^{id})_{P^*} = \int_{P^*}^P (\bar{V} - \bar{V}^{id})dP \quad (4.250)$$

Letting $P^* \rightarrow 0$ makes $\bar{G} \rightarrow \bar{G}^{id}$ and:

$$(\bar{G} - \bar{G}^{id})_P = \int_0^P (\bar{V} - \bar{V}^{id})dP \quad (4.251)$$

Using Eq. (4.248) for the real gas, Eq. (4.246) for the ideal gas and inserting them into Eq. (4.251) we have:

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_0^P (\bar{V} - \bar{V}^{id})dP \quad (\text{note: } \bar{G}^o \text{ is the same for both gases}) \quad (4.252)$$

Exponentiating both sides gives:

$$\phi \equiv \frac{f}{P} = \exp \left[\frac{1}{RT} \int_0^P (\bar{V} - \bar{V}^{id})dP \right] \quad (4.253)$$

where ϕ is called the fugacity coefficient. Next we introduce the molar volumes for the real and ideal gases (see Eqs. (1.6) and (1.26)):

$$\bar{V} = \frac{RTZ}{P} \quad \text{and} \quad \bar{V}^{id} = \frac{RT}{P}$$

When these are inserted into Eq. (4.253), we get:

$$\phi = \frac{f}{P} = \exp \left[\frac{1}{RT} \int_0^P \left(\frac{RTZ}{P} - \frac{RT}{P} \right) dP \right] = \exp \left[\int_0^P \frac{Z-1}{P} dP \right] \quad (4.254)$$

Note: The compressibility factor Z depends on pressure, $Z = Z(P)$.

Example. What is the expression for the fugacity when the compressibility factor is expanded as a power series?

Solution. The power series expansion is given by Eq. (1.17):

$$Z = 1 + B'P + C'P^2 + \dots$$

Inserting this into Eq. (4.254), we get:

$$\begin{aligned} f &= P \exp \left[\int_0^P \frac{Z-1}{P} dP \right] = P \exp \left[\int_0^P \frac{B'P + C'P^2 + \dots}{P} dP \right] \\ &= P \exp \left[\int_0^P (B' + C'P + \dots) dP \right] = P \exp \left[B'P + \frac{C'P^2}{2} + \dots \right] \end{aligned}$$

Example. What is the expression for the fugacity of a van der Waals gas?

Solution. The compressibility factor of a van der Waals gas is given by Eq. (1.26):

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) P \text{ (to first order in } P \text{)}$$

Just like in the previous example, we insert the expression for Z into Eq. (4.254):

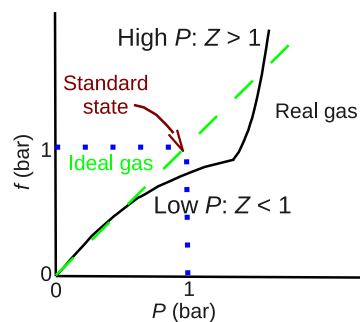
$$\begin{aligned} f &= P \exp \left[\int_0^P \frac{Z-1}{P} dP \right] = P \exp \left[\frac{1}{RT} \int_0^P \left(b - \left(\frac{a}{RT} \right) \right) dP \right] \\ &= P \exp \left[\frac{P}{RT} \left(b - \frac{a}{RT} \right) \right] \end{aligned}$$

Example. Given that the van der Waals constants of N_2 are $a = 1.408 \text{ L}^2 \text{ bar mol}^{-2}$ and $b = 0.03913 \text{ L mol}^{-1}$, estimate the fugacity of the gas at 50 bar and 298 K.

Solution. Insert the constants into the above expression (previous example):

$$\begin{aligned} f &= P \exp \left[\frac{P}{RT} \left(b - \frac{a}{RT} \right) \right] \\ &= (50 \text{ bar}) \times \exp \left\{ \left(\frac{50 \text{ bar}}{(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right) \right. \\ &\quad \times \left. \left[(0.03913 \text{ L mol}^{-1}) - \frac{1.408 \text{ L}^2 \text{ bar mol}^{-2}}{(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right] \right\} \\ &= 48.2 \text{ bar} \end{aligned}$$

Note: All thermodynamic tables refer to the ideal gas pressure P instead of the fugacity. In general, the fugacity can be either smaller (at low P) or higher than (at high P) the true pressure P . This can be seen by inspecting the graph shown in the first chapter where we plotted Z as a function of P . There Z may take values on either side of 1, which may make the exponent term in the fugacity expression (Eq. (4.254)) either negative, zero, or positive.



Even though we have not discussed the chemical potential in detail yet, we conclude that the same idea can be applied to the chemical potential as well (cf. Eq. (4.248)):

$$\mu_i = \mu_i^\circ + RT \ln(a_i) \quad (4.255)$$

where μ_i is the chemical potential and a_i is the activity. The activity is dimensionless, and $a_i = 1$ in the reference state for which $\mu_i = \mu_i^\circ$.

For real gases:
$$a_i = \frac{f_i}{P^\circ}$$

For ideal gases:
$$a_i = \frac{P_i}{P^\circ}$$

For pure liquids and solids ($P \propto P^\circ$):
$$a_i \approx 1$$

If the molar volume is assumed to be constant (i.e., liquids and solids), we can integrate one of the Maxwell equations (Eq. (4.228)):

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T, \{n_i\}} = \bar{V}_i$$

Integration of this expression yields:

$$\mu_i(T, P) = \mu_i^\circ + \bar{V}_i (P - P^\circ) \quad (4.256)$$

Note that we assumed that T and V are constants during the integration over P . Comparison of Eqs. (4.256) with (4.255) shows that:

$$\begin{aligned} RT \ln(a_i) &= \bar{V}_i (P - P^\circ) \\ \Rightarrow a_i &= e^{\bar{V}_i (P - P^\circ) / (RT)} \end{aligned} \quad (4.257)$$

Later we will see that when dealing with solutions, we write activity as a product of activity coefficient and concentration.

4.6 The significance of the chemical potential

Recall that we did not carry out Legendre transformation with respect to n_i and μ_i . Thus U , H , A and G behave exactly the same way with respect to these variables. Collecting the results from Eqs. (4.205), (4.211), (4.217) and (4.223):

$$\begin{aligned}\mu_i &= \left(\frac{\partial U}{\partial n_i} \right)_{S,V,\{n_i\}_{i \neq j}} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,\{n_i\}_{i \neq j}} \\ &= \left(\frac{\partial A}{\partial n_i} \right)_{T,V,\{n_i\}_{i \neq j}} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,\{n_i\}_{i \neq j}}\end{aligned}\quad (4.258)$$

The last definition based on the Gibbs energy is the most convenient because it is easy to hold T and P constant in practical applications.

Consider a single species which is distributed in two different phases. An example of such system is liquid water and water vapor. Let us denote the amount of substance in phase α as n_α and the amount of substance in phase β as n_β . The corresponding chemical potentials are denoted by μ_α and μ_β . When an infinitesimal amount of substance is transferred between the phases, we have $-dn_\alpha = dn_\beta \equiv dn$ (what leaves α must enter β and vice versa). According to Eq. (4.258), differential of the Gibbs energy is (constant T and P):

$$(dG)_{T,P} = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta = (\mu_\beta - \mu_\alpha) dn \quad (4.259)$$

Recall that for a spontaneous process $dG < 0$. Consider five different cases:

1. $dn > 0$ (i.e. substance moves from α to β) and $\mu_\beta < \mu_\alpha$. This fulfills the dG requirement for a spontaneous process. Substance moves from the phase with higher chemical potential to the phase where the chemical potential is lower.
2. $dn > 0$ (i.e. substance moves from α to β) and $\mu_\beta > \mu_\alpha$. dG would be positive and therefore this process is not spontaneous.
3. $dn < 0$ (i.e. substance moves from β to α) and $\mu_\beta < \mu_\alpha$. dG would be positive and therefore this process is not spontaneous.
4. $dn < 0$ (i.e. substance moves from β to α) and $\mu_\beta > \mu_\alpha$. This fulfills the dG requirement for a spontaneous process. Substance moves from the phase with higher chemical potential to the phase where the chemical potential is lower.
5. $dn = 0$ (i.e. nothing transferred) or $\mu_\alpha = \mu_\beta$ (i.e. chemical potentials equal). This corresponds to equilibrium ($dG = 0$). Such an equilibrium can exist even if the phases are at different pressures.

Measurement of μ_i as a function of P and T can be used to determine the molar entropy and the molar volume. To do this, we use the Maxwell relations (derivation is similar to Eqs. (4.226) - (4.228)):

$$-\bar{S}_i = -\left(\frac{\partial S}{\partial n_i}\right) = \left(\frac{\partial \mu_i}{\partial T}\right)_{P, \{n_i\}} \quad (4.260)$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right) = \left(\frac{\partial \mu_i}{\partial P}\right)_{T, \{n_i\}} \quad (4.261)$$

Example. Consider a mixture of ideal gases. What are the expressions for the chemical potentials and the partial molar entropies?

Solution. For simplicity we carry out the calculation for two species. Extension to many species is straight forward. We will show this in three parts:

1. Prove that the molar volume of the mixture (V) is equal to the partial molar volumes of the components (V_1 and V_2).
2. Use Eq. (4.228) to obtain $(\partial \mu_i / \partial P_i)$.
3. Integrate the resulting expression to obtain μ_i .

Step #1. First we note that the total number of gas atoms/molecules is given by $n = n_1 + n_2$, the total pressure $P = P_1 + P_2$ where each gas follows its own ideal gas law $P_i V = n_i R T$. There is no interaction between gas atoms/molecules in an ideal gas and therefore we can add up all these individual ideal gas equations to get $V = \frac{n R T}{P}$. Now Eq. (1.43) $\Rightarrow \bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, \{n_j\}_{j \neq i}} = \frac{R T}{P} = \bar{V}$.

Step #2. By using Eq. (4.261), the above result, the chain rule and $P_i = x_i P$, we can write:

$$\begin{aligned} \bar{V} = \frac{R T}{P} = \bar{V}_i &= \left(\frac{\partial \mu_i}{\partial P}\right)_{T, \{n_i\}} = \left(\frac{\partial \mu_i}{\partial P_i} \times \frac{\partial P_i}{\partial P}\right)_{T, \{n_i\}} = x_i \left(\frac{\partial \mu_i}{\partial P_i}\right)_{T, \{n_i\}} \\ &\Rightarrow \left(\frac{\partial \mu_i}{\partial P_i}\right)_{T, \{n_i\}} = \frac{R T}{P_i} \end{aligned} \quad (4.262)$$

Step #3. Integration of the above equation gives:

$$\begin{aligned} \int_{\mu_i^\circ}^{\mu_i} d\mu_i &= R T \int_{P^\circ}^{P_i} \frac{dP_i}{P_i} \\ \mu_i &= \mu_i^\circ + R T \ln \left(\frac{P_i}{P^\circ}\right) \end{aligned} \quad (4.263)$$

By differentiating Eq. (4.263) with respect to T and using Eq. (4.260) we get:

$$\bar{S}_i = \bar{S}_i^\circ - R \ln \left(\frac{P_i}{P^\circ} \right) \quad (4.264)$$

The same equation for pure ideal gas was derived earlier: $\bar{S} = \bar{S}^\circ - R \ln \left(\frac{P}{P^\circ} \right)$.

Note: The chemical potential is one of the most important concepts in chemical thermodynamics. In both chemical reactions and phase changes, the chemical potential of a species times its differential amount (reacted or transferred) determines the change in U , H , A , or G , depending on the variables that are held constant during the process.

4.7 Additivity of partial molar properties

In the following we will derive partial molar properties for U , A , G , S , V and H at constant P and T .

1. Partial molar Gibbs energy

Eq. (4.258) states that the chemical potential μ_i is the partial molar Gibbs energy:

$$G = \sum_{i=1}^{N_s} n_i \mu_i = \sum_{i=1}^{N_s} \left(\frac{\partial G}{\partial n_i} \right)_{T,P,\{n_j\}_{i \neq j}} \times n_i = \sum_{i=1}^{N_s} n_i \bar{G}_i$$

This is in agreement with the definition (i.e. Eqs. (1.42) and (1.43)). Note that T and P are constant.

2. Partial molar entropy

Differentiation of both sides of the above equation with respect to $-T$ gives:

$$\begin{aligned} \underbrace{- \left(\frac{\partial G}{\partial T} \right)_{P,\{n_i\}}}_{=S \text{ (Eq. (4.221))}} &= - \sum_{i=1}^{N_s} n_i \underbrace{\left(\frac{\partial \mu_i}{\partial T} \right)_{P,\{n_i\}}}_{=- \left(\frac{\partial S}{\partial n_i} \right), \text{ Eq. (4.227)}} \\ \Rightarrow S &= \sum_{i=1}^{N_s} n_i \left(\frac{\partial S}{\partial n_i} \right)_{T,P,\{n_j\}_{j \neq i}} = \sum_{i=1}^{N_s} \bar{S}_i n_i \end{aligned}$$

This is consistent with Eqs. (1.42) and (1.43).

3. Partial molar volume

Eq. (4.222) reads: $V = \left(\frac{\partial G}{\partial P} \right)_{T, \{n_i\}}$

Eqs. (1.43) and (4.261) give: $\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, \{n_i\}}$

Differentiation of the Gibbs energy equation on the previous page with respect to P gives (“the Gibbs energy Eq. differentiated”; cf. Eqs. (1.42) and (1.43)):

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, \{n_i\}} = \sum_{i=1}^{N_s} n_i \left(\frac{\partial \mu_i}{\partial P} \right)_{T, \{n_i\}} = \sum_{i=1}^{N_s} \bar{V}_i n_i \quad (4.265)$$

4. Partial molar enthalpy

Recall that: $H = G + TS$. Since both G and S are additive:

$$\begin{aligned} H = G + TS &= \sum_{i=1}^{N_s} n_i \bar{G}_i + T \sum_{i=1}^{N_s} n_i \bar{S}_i = \sum_{i=1}^{N_s} n_i \left(\frac{\partial G}{\partial n_i} + T \frac{\partial S}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} \quad (4.266) \\ &= \sum_{i=1}^{N_s} n_i \left(\frac{\partial (G + TS)}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} = \sum_{i=1}^{N_s} n_i \left(\frac{\partial H}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} \end{aligned}$$

Note: The same additivity properties hold for U and A as well.

How do ideal mixtures of gases behave?

By ideal mixture we mean that the gases do not interact with each other and hence they have their independent equations of state. Consider an alternative form of Eq. (4.263):

$$\mu_i = \mu_i^\circ + RT \ln \left(\frac{P_i}{P^\circ} \right) = \mu_i^\circ + RT \ln \left(\frac{y_i P}{P^\circ} \right) \quad (4.267)$$

where y_i is the mole fraction and P is the total pressure (this will be used below).

1. The total Gibbs energy of an ideal gas mixture

$$\begin{aligned} G &= \sum_{i=1}^{N_s} n_i \mu_i = \sum_{i=1}^{N_s} n_i \left(\mu_i^\circ + RT \ln \left(\frac{y_i P}{P^\circ} \right) \right) = \sum_{i=1}^{N_s} n_i \mu_i^\circ + RT \sum_{i=1}^{N_s} n_i \ln(y_i) \quad (4.268) \\ &+ RT \ln \left(\frac{P}{P^\circ} \right) \sum_{i=1}^{N_s} n_i = n \left(\sum_{i=1}^{N_s} y_i \mu_i^\circ + RT \sum_{i=1}^{N_s} y_i \ln(y_i) + RT \ln \left(\frac{P}{P^\circ} \right) \underbrace{\sum_{i=1}^{N_s} y_i}_{=1} \right) = n \bar{G} \end{aligned}$$

where $n = n_1 + \dots + n_{N_s}$ and $\bar{G} = G/n$ is the molar Gibbs energy of the mixture.

Note: Expressions for S , V , U , H and A can be obtained from this equation by using the relations connecting these variables to each other.

2. The total entropy of an ideal mixture

$$\begin{aligned}
 S &= - \left(\frac{\partial G}{\partial T} \right)_{P, \{n_i\}} \quad (4.269) \\
 &= - \left[\sum_{i=1}^{N_s} n_i \overbrace{\left(\frac{\partial \mu_i^\circ}{\partial T} \right)}^{=-\bar{S}_i^\circ \text{ (Eq. (4.260))}} + R \sum_{i=1}^{N_s} n_i \ln(y_i) + R \ln \left(\frac{P}{P^\circ} \right) \sum_{i=1}^{N_s} n_i \right] \\
 &= n \left(\sum_{i=1}^{N_s} y_i \bar{S}_i^\circ - R \sum_{i=1}^{N_s} y_i \ln(y_i) - R \ln \left(\frac{P}{P^\circ} \right) \right) = n\bar{S}
 \end{aligned}$$

where $\bar{S} = S/n$ is the total molar entropy of the mixture.

3. The total enthalpy of an ideal mixture

At constant P and T , $H = H^\circ$ and Eqs. (4.268), (4.269), (4.258) and (1.43) give:

$$\begin{aligned}
 H &= H^\circ = G^\circ + TS^\circ = \sum_{i=1}^{N_s} n_i (\mu_i^\circ + T\bar{S}_i^\circ) \quad (4.270) \\
 &= \sum_{i=1}^{N_s} n_i \left(\frac{\partial G^\circ}{\partial n_i} + T \frac{\partial S^\circ}{\partial n_i} \right)_{T, P, \{n_j\}_{j \neq i}} = \sum_{i=1}^{N_s} n_i \left(\frac{\partial H^\circ}{\partial n_i} \right) = \sum_{i=1}^{N_s} n_i \bar{H}_i^\circ
 \end{aligned}$$

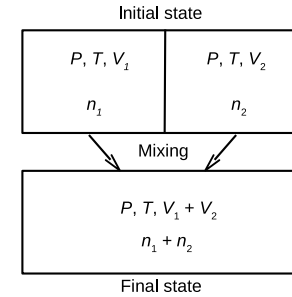
Note: The expression is independent of pressure (i.e. non-interacting gases).

4. The volume of an ideal gas mixture

Direct calculation gives ($n = n_1 + \dots + n_{N_s}$, $P = P_1 + \dots + P_{N_s}$):

$$V = \frac{nRT}{P} = \sum_{i=1}^{N_s} \underbrace{\frac{RT}{P}}_{\equiv (\partial V / \partial n_i)} n_i = \sum_{i=1}^{N_s} n_i \underbrace{\left(\frac{\partial V}{\partial n_i} \right)}_{=\bar{V}_i} = \sum_{i=1}^{N_s} n_i \bar{V}_i \quad (4.271)$$

Example. Consider mixing of two ideal gases as follows:



What are the initial values and the changes in Gibbs energy, entropy, enthalpy, and volume?

Solution. The initial values (i.e. before mixing) for the thermodynamic quantities in question are given by (separate systems):

$$\begin{aligned}
 G_{ini} &= n_1\mu_1 + n_2\mu_2 \quad \xrightarrow{\text{Eq. (4.263)}} \quad n_1\mu_1^\circ + n_1RT \ln \left(\frac{P}{P^\circ} \right) + n_2\mu_2^\circ + n_2RT \ln \left(\frac{P}{P^\circ} \right) \\
 S_{ini} &= n_1\bar{S}_1 + n_2\bar{S}_2 \quad \xrightarrow{\text{Eq. (4.264)}} \quad n_1\bar{S}_1^\circ - n_1R \ln \left(\frac{P}{P^\circ} \right) + n_2\bar{S}_2^\circ - n_2R \ln \left(\frac{P}{P^\circ} \right) \\
 H_{ini} &= n_1\bar{H}_1^\circ + n_2\bar{H}_2^\circ \\
 V_{ini} &= n_1 \frac{RT}{P} + n_2 \frac{RT}{P}
 \end{aligned}$$

After mixing the thermodynamic quantities become:

$$\begin{aligned}
 G_{fin} &\xrightarrow{\text{Eq. (4.268)}} \overbrace{n_1\mu_1^\circ + n_1RT \ln \left(\frac{P}{P^\circ} \right) + n_2\mu_2^\circ + n_2RT \ln \left(\frac{P}{P^\circ} \right) + n_1RT \ln (y_1)}^{=G_{ini}} \\
 &+ n_2RT \ln (y_2) = G_{ini} + RT \left(n_1 \overbrace{\ln (y_1)}^{<0} + n_2 \overbrace{\ln (y_2)}^{<0} \right) = G_{ini} + \overbrace{\Delta_{mix}G}^{<0 \text{ (spontaneous)}}
 \end{aligned}$$

$$\begin{aligned}
 S_{fin} &\xrightarrow{\text{Eq. (4.269)}} \underbrace{n_1\bar{S}_1^\circ - n_1R \ln \left(\frac{P}{P^\circ} \right) + n_2\bar{S}_2^\circ - n_2R \ln \left(\frac{P}{P^\circ} \right)}_{=S_{ini}} \\
 -Rn_1 \ln (y_1) - Rn_2 \ln (y_2) &= S_{ini} + \Delta_{mix}S \text{ (entropy increases)} \\
 &\quad \underbrace{\hspace{10em}}_{=\Delta_{mix}S > 0} \\
 H_{fin} &\xrightarrow{\text{Eq. (4.270)}} n_1\bar{H}_1^\circ + n_2\bar{H}_2^\circ = H_{fin} \Rightarrow \Delta_{mix}H = 0 \\
 V_{fin} &\xrightarrow{\text{Eq. (4.271)}} n_1 \frac{RT}{P} + n_2 \frac{RT}{P} = V_{ini} \Rightarrow \Delta_{mix}V = 0
 \end{aligned}$$

4.8 Gibbs-Duhem Equation

In this section we derive the Gibbs-Duhem equation, which we will need later. First we use Eq. (4.208) constant T and P :

$$U(V, S, \{n_i\}) = \sum_{i=1}^{N_s} n_i \mu_i - PV + ST$$

If we let each quantity vary in forming the corresponding differential dU , we get:

$$dU = \sum_{i=1}^{N_s} n_i d\mu_i + \sum_{i=1}^{N_s} \mu_i dn_i - PdV - VdP + SdT + TdS$$

On the other hand, the total derivative of U in Eq. 4.203) gives:

$$dU = \sum_{i=1}^{N_s} \mu_i dn_i - PdV + TdS$$

By subtracting the two equations from each other yields:

$$\sum_{i=1}^{N_s} n_i d\mu_i - VdP + SdT = 0 \quad (4.272)$$

This is known as *the Gibbs-Duhem equation*. We will use it later when we discuss the Clapeyron equation as well as Henry's and Raoult's laws.

Notes:

1. At constant P and T , Eq. (4.272) becomes: $\sum_{i=1}^{N_s} n_i d\mu_i = 0$.
2. For a system with two species at constant T and P we have (y_1 and y_2 are the mole fractions for species 1 and 2):

$$\begin{aligned} y_1 d\mu_1 + y_2 d\mu_2 &= 0 \quad (\text{with } y_2 = 1 - y_1) \\ \Rightarrow y_1 d\mu_1 + (1 - y_1) d\mu_2 &= 0 \end{aligned} \quad (4.273)$$

(conservation of chemical potential)

4.9 Additional applications of Maxwell relations

First we consider Maxwell relations for a pure system (i.e., only one species). The equations can be derived using U , H , A or G :

$$\left(\frac{\partial T}{\partial \bar{V}}\right)_{\bar{S}} \stackrel{\text{Eq. (4.205)}}{=} \left(\frac{\partial^2 \bar{U}}{\partial \bar{V} \partial \bar{S}}\right) \stackrel{\text{x-change OK}}{=} \left(\frac{\partial^2 \bar{U}}{\partial \bar{S} \partial \bar{V}}\right) \stackrel{\text{Eq. (4.205)}}{=} \left(\frac{\partial P}{\partial \bar{S}}\right)_{\bar{V}} \quad (4.274)$$

$$\left(\frac{\partial T}{\partial P}\right)_{\bar{S}} \stackrel{\text{Eq. (4.211)}}{=} \left(\frac{\partial^2 \bar{H}}{\partial P \partial \bar{S}}\right) \stackrel{\text{x-change OK}}{=} \left(\frac{\partial^2 \bar{H}}{\partial \bar{S} \partial P}\right) \stackrel{\text{Eq. (4.211)}}{=} \left(\frac{\partial \bar{V}}{\partial \bar{S}}\right)_P \quad (4.275)$$

$$\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T \stackrel{\text{Eq. (4.215)}}{=} \left(\frac{\partial^2 \bar{A}}{\partial \bar{V} \partial T}\right) \stackrel{\text{x-change OK}}{=} \left(\frac{\partial^2 \bar{A}}{\partial T \partial \bar{V}}\right) \stackrel{\text{Eq. (4.216)}}{=} \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} \quad (4.276)$$

$$-\left(\frac{\partial \bar{S}}{\partial P}\right)_T \stackrel{\text{Eq. (4.221)}}{=} \left(\frac{\partial^2 \bar{G}}{\partial P \partial T}\right) \stackrel{\text{x-change OK}}{=} \left(\frac{\partial^2 \bar{G}}{\partial T \partial P}\right) \stackrel{\text{Eq. (4.222)}}{=} \left(\frac{\partial \bar{V}}{\partial T}\right)_P \quad (4.277)$$

When a number of different species are present, the chemical potential must be included. For example for the internal energy U , the following Maxwell relations can be written (similar relations exist also for H , A and G):

$$\left(\frac{\partial T}{\partial n_i}\right)_{S,V,\{n_j\}_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial S}\right)_{V,\{n_i\}} \quad (4.278)$$

$$-\left(\frac{\partial P}{\partial n_i}\right)_{S,V,\{n_j\}_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial V}\right)_{S,\{n_i\}} \quad (4.279)$$

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{S,V,\{n_k\}_{k \neq j}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{S,V,\{n_k\}_{k \neq i}} \quad (4.280)$$

Example. Calculate $(\partial \bar{U} / \partial \bar{V})_T$ for a real gas.

Solution. Earlier we have shown that $(\partial \bar{U} / \partial \bar{V})_T = 0$ for an ideal gas. If the equation of state of the real gas is known in terms of P , we will be able to use the following equation to calculate the partial derivative:

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} - P \quad (4.281)$$

To show that this result holds, we first combine the 1st and 2nd laws of thermodynamics (reversible process):

1st law: $dU = dq_{rev} + dw_{rev} = dq_{rev} - PdV$ (if only PV -work)

2nd law: $dS = \frac{dq_{rev}}{T}$

Combined: $dU = TdS - PdV$

By considering molar quantities in above, dividing both sides of the equation by $d\bar{V}$, and imposing constant temperature gives:

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T \left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T - P \quad (4.282)$$

Now Eq. (4.276) allows us to write this as:

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} - P$$

Example. This equation can be applied to a van der Waals gas. In this case the pressure can be written as (Eq. (1.24)):

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

Differentiation of P with respect T gives: $\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V} - b}$

Substitution of this derivative in Eq. (4.281) gives the partial derivative:

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right) = \frac{RT}{\bar{V} - b} - P = \frac{RT}{\bar{V} - b} - \left(\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}\right) = \frac{a}{\bar{V}^2} \quad (4.283)$$

Integration of this equation yields the change in internal energy for a given change in volume at constant temperature:

$$\Delta \bar{U} = \int_{\bar{U}_1}^{\bar{U}_2} d\bar{U} = \int_{\bar{V}_1}^{\bar{V}_2} \frac{a}{\bar{V}^2} d\bar{V} = a \left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}_2} \right)$$

Example. Propane gas is allowed to expand isothermally from 10 to 30 L/mol. What is the change in the molar internal energy? Use the van der Waals equation with $a = 8.779 \text{ L}^2 \text{ bar mol}^{-2}$.

Solution. First we have to convert the value of a into SI units:

$$\begin{aligned} a &= (8.779 \text{ L}^2 \text{ bar mol}^{-2}) \times (10^5 \text{ Pa bar}^{-1}) \times (10^{-3} \text{ m}^3 \text{ L}^{-1})^2 \\ &= 0.8779 \text{ Pa m}^6 \text{ mol}^{-2} \end{aligned}$$

Then we can use the expression for ΔU on the previous page:

$$\Delta \bar{U} = a \left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}_2} \right) = (0.8779 \text{ Pa m}^6 \text{ mol}^{-2}) \\ \times \left(\frac{1}{10 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} - \frac{1}{30 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} \right) = 58.5 \text{ J mol}^{-1}$$

Example. What is the change in the molar entropy when a van der Waals gas expands isothermally?

Solution. First we use one of the Maxwell relations (Eq. (4.276)) and then we integrate both sides of the resulting equation (see also the previous example):

$$\left(\frac{\partial \bar{S}}{\partial \bar{V}} \right)_T \stackrel{\text{Eq. (4.276)}}{=} \left(\frac{\partial P}{\partial T} \right)_{\bar{V}} = \frac{R}{\bar{V} - b} \\ \int_{\bar{S}_1}^{\bar{S}_2} d\bar{S} = R \int_{\bar{V}_1}^{\bar{V}_2} \frac{d\bar{V}}{\bar{V} - b} \Rightarrow \Delta \bar{S} = R \ln \left(\frac{\bar{V}_2 - b}{\bar{V}_1 - b} \right)$$

Cubic and isothermal expansion coefficients

The cubic expansion coefficient is defined as (“how the volume of a substance changes with temperature”):

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T} \right)_P \quad (4.284)$$

The isothermal compressibility coefficient is defined as (“how the volume of a substance changes with pressure”):

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial P} \right)_T \quad (4.285)$$

For an ideal gas these quantities are $\alpha = 1/T$ and $\kappa = 1/P$. These constants can also be used in simplifying thermodynamic expressions. For example:

$$\left(\frac{\partial P}{\partial T} \right)_{\bar{V}} = -\frac{(\partial \bar{V} / \partial T)_P}{(\partial \bar{V} / \partial P)_T} = \frac{\alpha}{\kappa} \quad (4.286)$$

and further:

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}} \right)_T \stackrel{\text{Eq. (4.281)}}{=} \frac{\alpha T - \kappa P}{\kappa} \quad (4.287)$$

Dependency of enthalpy on the pressure at constant temperature

We are seeking an expression like Eq. (4.281) that would help us to calculate the dependency of enthalpy on pressure. Both sides of the differential $dH = TdS + VdP$ can be divided by pressure at constant T to obtain:

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = T \left(\frac{\partial \bar{S}}{\partial P}\right)_T + \bar{V} \quad (4.288)$$

Using one of the Maxwell relations (Eq. (4.226)), we can modify this equation to:

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = -T \left(\frac{\partial \bar{V}}{\partial T}\right)_P + \bar{V} \quad (4.289)$$

The relation between constant pressure and constant volume heat capacities

In Eq. (2.116) we found the following relation:

$$\bar{C}_P - \bar{C}_V = \left[P + \left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T \right] \left(\frac{\partial \bar{V}}{\partial T}\right)_P \quad (4.290)$$

From Eqs. (4.284), (4.285) and (4.287) we can now get:

$$\bar{C}_P - \bar{C}_V = \frac{T\bar{V}\alpha^2}{\kappa} \quad (4.291)$$

Note that often it is more difficult to measure C_V than C_P experimentally. If C_P is known, the above equation gives C_V .

Chapter 5: Chemical equilibrium

“Chemical reactions always attempt to approach equilibrium with an equilibrium constant given by the the standard reaction Gibbs energy”

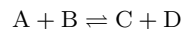
5.1 Derivation of the general equilibrium expression

207



Norwegian chemists: Cato Guldberg (1836 - 1902) and Peter Waage (1833 - 1900)

Experiments: Chemical reactions can approach equilibrium from either direction (CG & PW):



Thus it does not matter, if one mixes (A and B) or (C and D), the system will end up in the same equilibrium. Also they realized that the equilibrium depends on concentrations of A, B, C and D. Later van't Hoff (1877) suggested an expression for equilibrium, which depends on concentrations.

Recall Eq. (4.220): $dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i$

Remember that most chemical reactions are carried out at constant pressure and temperature and hence $dT = dP = 0$. Next, recall Eq. (2.135):

$$n_i = n_{i,0} + v_i \xi \quad (5.292)$$

where n_i is the amount of species i , $n_{i,0}$ is the initial amount of species i , v_i is the stoichiometric coefficient and ξ is the extent of reaction. Eq. (5.292) yields the differential $dn_i = v_i d\xi$. Sometimes we use the “scaled” version of Eq. (5.292): $n_i = n_{i,0} + v_i n_{i,0} \xi$ where ξ is now strictly between 0 and 1.

208

If one chemical reaction is considered, substitution of the differential into Eq. (4.220) gives:

$$dG = -SdT + VdP + \left(\sum_{i=1}^{N_s} v_i \mu_i \right) d\xi \quad (5.293)$$

At specified fixed T and P :

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_{i=1}^{N_s} v_i \mu_i \quad (5.294)$$

In chemical equilibrium G has its minimum value and hence: $\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$

Implying this condition to Eq. (5.294), we get the equilibrium condition:

$$\sum_{i=1}^{N_s} v_i \mu_{i,eq} = 0 \quad (5.295)$$

This is equilibrium condition applies to all chemical equilibria (gases, liquids, solids, or solutions).

In similar fashion to Eq. (2.137), we define the reaction Gibbs energy $\Delta_r G$:

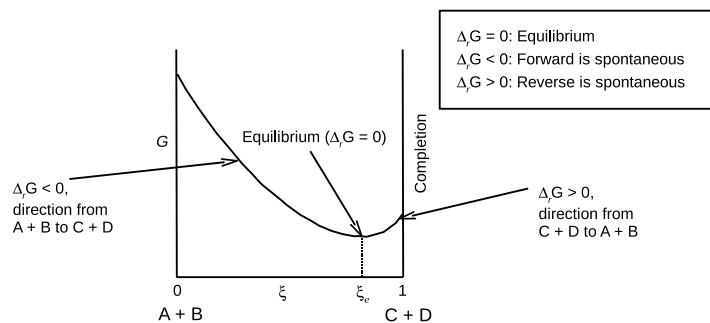
$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} \quad (5.296)$$

By combining the equilibrium condition, Eqs. (5.294) and (5.296):

$$\Delta_r G = \sum_{i=1}^{N_s} v_i \mu_i \quad (5.297)$$

The reaction Gibbs energy at a given value of ξ , tells us how much the Gibbs energy changes when ξ is varied. Its value approaches zero when close to the equilibrium.

Consider reaction: $A + B \rightleftharpoons C + D$



Note: Usually Δ denotes a difference but here it denotes a derivative. However, there is a close connection to differences in chemical potentials via Eq. (5.297).

To proceed towards the concept of equilibrium constant, recall Eq. (4.255):

$$\mu_i = \mu_i^\circ + RT \ln(a_i)$$

where μ_i° is the standard chemical potential and a_i is activity of species i . In equilibrium, this equation can be written as ($a_{i,eq} = a_i(\xi_{eq})$):

$$\mu_{i,eq} = \mu_i^\circ + RT \ln(a_{i,eq}) \quad (5.298)$$

Inserting this into the equilibrium condition, Eq. (5.295), gives:

$$\sum_{i=1}^{N_s} v_i \mu_i^\circ = -RT \sum_{i=1}^{N_s} v_i \ln(a_{i,eq}) \quad (5.299)$$

Using the rules of algebra for logarithms, this can be rewritten:

$$\sum_{i=1}^{N_s} v_i \mu_i^\circ = -RT \sum_{i=1}^{N_s} \ln(a_{i,eq}^{v_i}) \quad (5.300)$$

and further (“a sum of logarithms is a logarithm of products”):

$$\underbrace{\sum_{i=1}^{N_s} v_i \mu_i^\circ}_{=\Delta_r G^\circ} = -RT \ln \left(\underbrace{\prod_{i=1}^{N_s} a_{i,eq}^{v_i}}_{\equiv K} \right) = -RT \ln(K) \quad (5.301)$$

Note: $\Delta_r G^\circ$ is a plain number, which comes from the standard chemical potentials of the isolated species A, B, C, D whereas $\Delta_r G$ is a function depending on ξ . The value of $\Delta_r G^\circ$ depends only on the species which react but not on the details of the reaction itself. $\Delta_r G$ describes the reaction.

Thus we can summarize the previous result as:

$$\Delta_r G^\circ = -RT \ln(K) \quad (5.302)$$

The equilibrium constant K is directly related to the standard reaction Gibbs energy $\Delta_r G^\circ$. Because $\Delta_r G^\circ$ is a function of temperature only (pressure fixed to 1 bar), the equilibrium constant K depends only on temperature. Note that K is a dimensionless quantity.

Let's consider a *non-equilibrium condition* (i.e. $\Delta_r G \neq 0$) and rewrite Eqs. (5.297) and (5.298) as:

$$\Delta_r G = \sum_{i=1}^{N_s} v_i \mu_i^\circ + RT \sum_{i=1}^{N_s} v_i \ln(a_i) = \Delta_r G^\circ + RT \ln \underbrace{\left(\prod_{i=1}^{N_s} a_i^{v_i} \right)}_{\equiv Q} = \Delta_r G^\circ + RT \ln(Q) \quad (5.303)$$

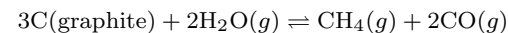
where we have defined reaction quotient Q . It is a very similar quantity to K but it is a dynamic variable that describes a non-equilibrium situation. At equilibrium, $Q = K$ and in general $Q = Q(\xi)$ whereas K does not depend on ξ . By calculating the reaction quotient Q , it is possible to determine the direction in which the chemical reaction would proceed at given ξ . Substitution of the definition of the Gibbs energy ($G = H - TS$) into Eq. (5.296) gives:

$$\Delta_r G = \left(\frac{\partial H}{\partial \xi} \right)_{T,P} - T \left(\frac{\partial S}{\partial \xi} \right)_{T,P} = \Delta_r H - T \Delta_r S \quad (5.304)$$

Note that the previous definition is in agreement with Eqs. (2.137). The same equation also applies when the reactants and products are in their standard states:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (5.305)$$

Example. Write expressions for K and Q for the following reaction:



By applying Eqs. (5.301) and (5.303) we have:

$$K = \left(\frac{a_{\text{CH}_4} a_{\text{CO}}^2}{a_{\text{C}}^3 a_{\text{H}_2\text{O}}^2} \right) \text{ where the activities are evaluated at equilibrium } (\xi_{eq})$$

$$Q(\xi) = \left(\frac{a_{\text{CH}_4} a_{\text{CO}}^2}{a_{\text{C}}^3 a_{\text{H}_2\text{O}}^2} \right) \text{ where the activities are evaluated at a given point } \xi$$

Also $Q(\xi_{eq}) = K$.

5.2 Equilibrium constant expressions for gas reactions

Recall that for real gases the activity is given by (see Eqs. (4.248) and (4.255)): $a_i = \frac{f_i}{P^\circ}$ where P° is the standard state pressure (1 bar) and fugacity is given, for example, by Eq. (4.254):

$$f_i = P_i \exp \left(\int_0^{P_i} \frac{Z - 1}{P} dP \right)$$

and Z is the compressibility factor of the gas. At equilibrium Eq. (5.301) now gives:

$$K = \prod_{i=1}^{N_s} a_{i,eq}^{v_i} = \prod_{i=1}^{N_s} \left(\frac{f_{i,eq}}{P^\circ} \right)^{v_i} \quad (5.306)$$

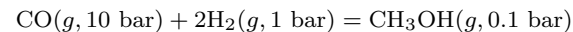
For ideal gases Eq. (5.306) can be written as follows ($a_i = P_i/P^\circ$, see Eq. (4.255)):

$$K = \prod_{i=1}^{N_s} \left(\frac{P_{i,eq}}{P^\circ} \right)^{v_i} \quad \text{and} \quad Q = \prod_{i=1}^{N_s} \left(\frac{P_i}{P^\circ} \right)^{v_i} \quad (5.307)$$

Notes:

- ▶ K depends only on partial pressures P_i and also on the total pressure P .
- ▶ As K depends on the way the stoichiometric coefficients are written, a full reaction equation must always be written when specifying K .
- ▶ K determines ξ_{eq} (the equilibrium extent of the reaction) via Eq. (5.301).

Example. A mixture of $\text{CO}(g)$ and $\text{CH}_3\text{OH}(g)$ at 500 K with $P_{\text{CO}} = 10$ bar, $P_{\text{H}_2} = 1$ bar, and $P_{\text{CH}_3\text{OH}} = 0.1$ bar is passed over a catalyst. The reaction occurring in the gas phase is:



where the standard reaction Gibbs energy is $\Delta_r G^\circ = 21.21 \text{ kJ mol}^{-1}$. In which direction would the reaction proceed? Assume that the gases behave according to the ideal gas law.

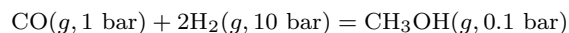
Solution. Recall that the the reaction Gibbs energy ($\Delta_r G$) tells us which way the reaction would proceed. If it is negative, the reaction proceeds spontaneously from left to right and if it is positive, the reaction proceeds spontaneously from right to left. If $\Delta_r G$ is zero, the reaction is in equilibrium. By using Eqs. (5.303) and (5.307) we get:

$$\Delta_r G = \Delta_r G^\circ + RT \ln(Q) = 21.21 \text{ kJ mol}^{-1} + (0.0083145 \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})$$

$$\times \ln \left(\frac{0.1}{10 \times 1^2} \right) = 2.07 \text{ kJ mol}^{-1} > 0$$

Thus the reaction is not spontaneous as written. Note that the only effect of P° 's in this calculation were to cancel the units since its numerical value was 1 bar. The stoichiometric coefficients are: $v_{\text{CO}} = -1$, $v_{\text{H}_2} = -2$ and $v_{\text{CH}_3\text{OH}} = 1$.

If the conditions had been chosen as follows:

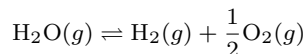


we would have:

$$\begin{aligned}\Delta_r G &= 21.21 \text{ kJ mol}^{-1} + (0.0083145 \text{ kJ K}^{-1} \text{ mol}^{-1}) (500 \text{ K}) \times \ln \left(\frac{0.1}{1 \times 10^2} \right) \\ &= -7.51 \text{ kJ mol}^{-1} < 0\end{aligned}$$

This means that the reaction would be thermodynamically spontaneous.

Example. Consider decomposition reaction of water:



The standard reaction Gibbs energy for this reaction is $118.08 \text{ kJ mol}^{-1}$ at 2300 K . What is the extent of reaction ξ_{eq} at 2300 K and at a total pressure of 1.00 bar ? Assume that gases behave according to the ideal gas law.

Solution. First we use Eq. (5.302) to get the equilibrium constant K :

$$\ln(K) = -\frac{\Delta_r G^\circ}{RT} = \frac{118080 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (2300 \text{ K})} = -6.175 \Rightarrow K = 2.08 \times 10^{-3}$$

In the following, the initial amount of water is denoted by n and initially all other concentrations are zero. At given extent of reaction ξ , the amount of each component is: $n_{\text{H}_2\text{O}} = (1 - \xi)n$, $n_{\text{H}_2} = \xi n$ and $n_{\text{O}_2} = \xi n/2$. Thus the total amount is $(1 - \xi)n + \xi n + \xi n/2 = n(1 + \xi/2)$ and the mole fractions are then: $y_{\text{H}_2\text{O}} = (1 - \xi)/(1 + \xi/2)$, $y_{\text{H}_2} = \xi/(1 + \xi/2)$ and $y_{\text{O}_2} = (\xi/2)/(1 + \xi/2)$. The partial pressures (P_i) can be calculated by multiplying the corresponding mole fraction by the total pressure P . Note that the choice of ξ is slightly different than in Eq. (5.292) (scaling $\xi = n\xi'$ so that ξ is now between 0 and 1). Then apply Eq. (5.307) to relate the partial pressures to K :

$$K = \frac{P_{\text{H}_2} \sqrt{P_{\text{O}_2}}}{P_{\text{H}_2\text{O}} \sqrt{P^\circ}} = \frac{\xi_{eq}^{3/2} \bar{P}^{1/2}}{(1 - \xi_{eq})(2 + \xi_{eq})^{1/2}} \text{ where } \bar{P} = P/P^\circ = (1 \text{ bar})/(1 \text{ bar}) = 1$$

$$K = \frac{\xi_{eq}^{3/2}}{(1 - \xi_{eq})(2 + \xi_{eq})^{1/2}} = 2.08 \times 10^{-3} \Rightarrow \xi_{eq} = 0.020 \text{ (numerical solution)}$$

(there are actually three roots: one real and two complex)

Therefore about 2% of H_2O is dissociated under the given conditions.

Example. Demonstrate that chemical reactions in the gas phase never go to completion. Assume ideal gas behavior as well as constant pressure and temperature.

Solution. Consider reaction $\text{A}(g) = \text{B}(g)$ at constant pressure. First calculate the Gibbs energy of the system as a function of the extent of reaction ξ (Eq. (5.293)):

$$dG = -S \underbrace{dT}_{=0} + V \underbrace{dP}_{=0} + \left(\sum_{i=1}^{N_s} v_i \mu_i(\xi) \right) d\xi = \mu_B(\xi) d\xi - \mu_A(\xi) d\xi$$

Using Eq. (4.255), the chemical potentials can be written as:

$$\begin{aligned} \mu_A &= \mu_A^\circ + RT \ln \left(\frac{P_A}{P^\circ} \right) = \mu_A^\circ + RT \ln \left(\frac{y_A P}{P^\circ} \right) \\ &= \mu_A^\circ + RT \left(\ln \underbrace{\left(\frac{y_A}{(1-\xi)n_{tot}/n_{tot}} \right)}_{=1-\xi} + \ln \left(\frac{P}{P^\circ} \right) \right) = \mu_A^\circ + RT \left(\ln(1-\xi) + \ln \left(\frac{P}{P^\circ} \right) \right) \\ \mu_B &= \mu_B^\circ + RT \left(\ln(\xi) + \ln \left(\frac{P}{P^\circ} \right) \right) \end{aligned}$$

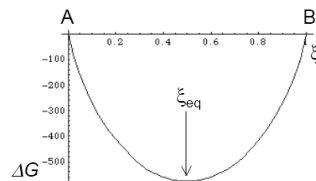
Inserting these results into the expression for dG , we get:

$$dG = \left\{ \underbrace{\Delta\mu_{BA}}_{=\mu_B^\circ - \mu_A^\circ} + RT \ln \left(\frac{\xi}{1-\xi} \right) \right\} d\xi$$

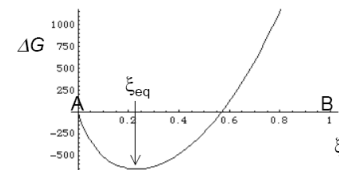
Integration of this equation from the initial point ($\xi = 0$) to ξ gives:

$$\begin{aligned} \int_{G(0)}^{G(\xi)} dG &= \int_0^\xi \left\{ \Delta\mu_{BA} + RT \ln \left(\frac{\xi}{1-\xi} \right) \right\} d\xi \Rightarrow \\ \Delta G(\xi) &= \xi \Delta\mu_{BA} + RT \int_0^\xi \ln \left(\frac{\xi}{1-\xi} \right) d\xi = \xi \Delta\mu_{BA} + RT \underbrace{((1-\xi) \ln(1-\xi) + \xi \ln(\xi))}_{=\Delta_{mix}G} \end{aligned}$$

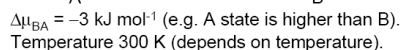
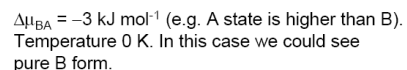
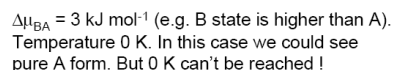
Consider the following examples (ΔG in units of J mol^{-1}):



$\Delta\mu_{BA} = 0$ - does not depend on temperature. Both forms are equally favored.



$\Delta\mu_{BA} = 3 \text{ kJ mol}^{-1}$ (e.g. B state is higher than A). Temperature 300 K (ξ_{eq} depends on temperature).



Only at 0 K we could have pure forms for A or B - depending which one is lower in energy! This applies to all chemical reactions. Thermal energy is the driving force driving a chemical reaction into equilibrium.

Consider a chemical reaction: $aA + bB \rightleftharpoons cC + dD$. If the initial concentrations/pressures $[A]_0$, $[B]_0$, $[C]_0$ and $[D]_0$ are known and one of $[A]$, $[B]$, $[C]$ or $[D]$ is known at equilibrium, it is possible to use the above balanced chemical equation to obtain concentrations of all of the species at equilibrium. This is because there is just one variable that describes the reaction (ξ ; the extent of reaction). Given the equilibrium concentrations/pressures for all the species, it is possible to derive an expression for K in terms of ξ_{eq} by using Eq. (5.307) and thus obtain a value for K using experimental data.

- ▶ measurement of gas density or pressure
- ▶ light absorption
- ▶ refractive index
- ▶ electrical conductivity

1. The measurement may not change any of the concentrations/pressures in the system - otherwise the measurement would change the equilibrium as well!
2. The same value for K should be obtained when the equilibrium is approached from either side.
3. The same value for K should be obtained over a wide range of initial concentrations.

The relation between K and ξ_{eq} :

We have already seen that the equilibrium constant K can be written in terms of ξ_{eq} (e.g., the water dissociation example). In the following we will consider a general equation of the form: $A \rightleftharpoons mB$ and derive a general expression for the equilibrium constant. The reaction is assumed to occur in the gas phase and all gaseous components should follow the ideal gas law. According to Eq. (5.307) the equilibrium constant can be written as:

$$K = \left(\frac{P_A}{P^\circ} \right)^{-1} \times \left(\frac{P_B}{P^\circ} \right)^m \quad (5.308)$$

Let us denote the total pressure by P and partial pressures of A and B by $P_A = y_A P$ and $P_B = y_B P$. The concentrations of A and B at equilibrium can be written in terms of ξ_{eq} (note the scaling of ξ):

$$n_{A,eq} = n_{A,0} (1 - \xi_{eq}) \quad \text{and} \quad n_{B,eq} = n_{A,0} \xi_{eq} m \quad (5.309)$$

$$\text{The total amount} = n_{A,eq} + n_{B,eq} = n_{A,0} (1 - \xi_{eq}) + n_{A,0} \xi_{eq} m$$

From this we can calculate the molar fractions and further the partial pressures P_A and P_B :

$$y_A = \frac{1 - \xi_{eq}}{1 - \xi_{eq} (1 - m)} \quad \text{and} \quad y_B = \frac{\xi_{eq}}{1 - \xi_{eq} (1 - m)} \quad (5.310)$$

$$P_A = P \times \frac{1 - \xi_{eq}}{1 - \xi_{eq} (1 - m)} \quad \text{and} \quad P_B = P \times \frac{\xi_{eq} m}{1 - \xi_{eq} (1 - m)} \quad (5.311)$$

Inserting these into the equilibrium constant expression, we get:

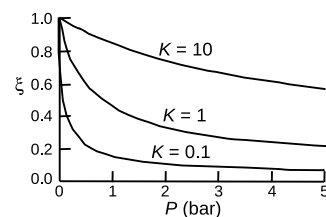
$$\begin{aligned} K &= \left(\frac{P}{P^\circ} \right)^{m-1} \times \left(\frac{1 - \xi_{eq}}{1 - \xi_{eq} (1 - m)} \right)^{-1} \times \left(\frac{\xi_{eq} m}{1 - \xi_{eq} (1 - m)} \right)^m \\ &= \left(\frac{P/P^\circ}{1 - \xi_{eq} (1 - m)} \right)^{m-1} \times \frac{(\xi_{eq} m)^m}{(1 - \xi_{eq})} \end{aligned} \quad (5.312)$$

If $m = 2$ (for example, $N_2O_4(g) = 2NO_2(g)$), this reduces to:

$$K = \frac{4\xi_{eq}^2 P/P^\circ}{1 - \xi_{eq}^2} \quad (5.313)$$

In this case, the equation can be also solved for ξ :

$$\xi_{eq} = \frac{1}{[1 + (4/K) (P/P^\circ)]^{1/2}} \quad (5.314)$$



Equilibrium extent of reaction as a function of pressure at various values of K .

The relation between ξ_{eq} and gas densities:

When $m > 1$, it is possible to determine the extent of reaction by measuring the density of the gas. For example, consider reaction $A = 2B$ and denote the mass of A by m_A and the molecular mass by M_A . Also assume that temperature and pressure are constant and that both A and B follow the ideal gas law. The initial volume before the reaction takes place is:

$$V_{ini} = \frac{m_A RT}{M_A P} \quad (\text{where we used } n = m_A/M_A) \quad (5.315)$$

At equilibrium we have a similar equation (the total mass is conserved in chemical reactions and we still use m_A below):

$$V_{eq} = \frac{m_A RT}{M_{eq} P} \quad \text{where } M_{eq} = y_A M_A + y_B M_B = y_A M_A + \frac{1}{2} y_B M_A \quad (5.316)$$

where we also used the fact that $M_A = 2M_B$ (the mass conservation restriction). Calculation of the ratios between the volumes gives:

$$\frac{V_{ini}}{V_{eq}} = \frac{M_{eq}}{M_A} = \frac{y_A M_A + \frac{1}{2} y_B M_A}{M_A} = \frac{1}{1 + \xi_{eq}} \quad (5.317)$$

with $y_A = \frac{1 - \xi_{eq}}{1 + \xi_{eq}}$ and $y_B = \frac{2\xi_{eq}}{1 + \xi_{eq}}$

Note that the mass conservation also relates the volumes to densities ρ :

$$\begin{cases} \rho_{ini} V_{ini} = m_A \\ \rho_{eq} V_{eq} = m_A \end{cases} \Rightarrow \frac{\rho_{eq}}{\rho_{ini}} = \frac{V_{ini}}{V_{eq}} \quad (5.318)$$

If we solve for ξ_{eq} on previous page, we get two useful results:

$$\xi_{eq} = \frac{M_A - M_{eq}}{M_{eq}} \quad \text{and} \quad \xi_{eq} = \frac{\rho_{ini} - \rho_{eq}}{\rho_{eq}} \quad (5.319)$$

Thus by measuring either the molar masses or gas densities before the reaction takes place and at the equilibrium, Eq. (5.319) can be used for calculating ξ_{eq} . Note that this derivation assumed a specific stoichiometry for the chemical equation.

Example. Consider reaction $N_2O_4(g) = 2NO_2(g)$ (molecular weight of N_2O_4 is 92.01 g mol^{-1}) at constant T (298.15 K) and P (1.0133 bar). 1.588 g of N_2O_4 dissociates and expands to 500 cm^3 volume. What is the extent of reaction ξ_{eq} and the equilibrium constant K ?

Solution. ξ_{eq} can be calculated using Eq. (5.319) with the molecular weights as follows:

$$M_{eq} = \frac{m_{N_2O_4} RT}{V_{eq} P} = \frac{(1.588 \text{ g}) (0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})}{(1.013 \text{ bar}) (0.5 \text{ L})} = 77.70 \text{ g mol}^{-1}$$

M_{ini} was given as 92.01 g mol^{-1} and now by applying Eq. (5.319) we get:

$$\xi_{eq} = \frac{M_{ini} - M_{eq}}{M_{eq}} = \frac{(92.01 \text{ g mol}^{-1}) - (77.70 \text{ g mol}^{-1})}{77.70 \text{ g mol}^{-1}} = 0.1842$$

The equilibrium constant can be obtained from Eq. (5.314):

$$K = \frac{4\xi_{eq}^2 (P/P^\circ)}{1 - \xi_{eq}^2} = \frac{4(0.1842)^2 (1.0133)}{1 - (0.1842)^2} = 0.143$$

For a more complicated reaction $A + 3B = 2C$, the following expression for the equilibrium constant can be obtained:

$$K = \frac{16\xi_{eq}^2 (1 - \xi_{eq})}{(1 - 3\xi_{eq})^3 (P/P^\circ)^2} \quad (5.320)$$

Each type of reaction requires its own expressions for K and ξ_{eq} but they can be derived by using the previously outlined approach.

Example. Consider the following reaction: $N_2(g) + 3H_2(g) = 2NH_3(g)$. What total pressure must be used to obtain 10% conversion of nitrogen to ammonia at 400°C ? Assume equimolar initial mixture of N_2 and H_2 and ideal gas behavior. The equilibrium constant for the reaction is 1.60×10^{-4} at standard pressure of 1 bar.

Solution. 10% conversion corresponds to $\xi_{eq} = 0.1$. We use Eq. (5.320):

$$P = P^\circ \left(\frac{16\xi_{eq}^2 (1 - \xi_{eq})}{(1 - 3\xi_{eq})^3 K} \right)^{1/2} = (1 \text{ bar}) \times \left(\frac{16 \times (0.1)^2 \times (1 - 0.1)}{(1 - 3 \times 0.1)^3 \times (1.60 \times 10^{-4})} \right)^{1/2}$$

$$= 51.2 \text{ bar}$$

Note: Calculation of the equilibrium compositions of a reaction system that contains two or more reactions is more complicated (results in many different equations instead of just one). Furthermore the equations are non-linear, which typically means that it is not possible to find analytic solutions. Numerical methods are the only way to proceed in such case (i.e., computers).

5.4 Calculation of equilibrium constants using standard Gibbs energies of formation 227

In general $\Delta_r G^\circ$ can be determined in three different ways:

1. Determine the equilibrium constant K experimentally and use Eq. (5.302).
2. By using Eq. (5.304): $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, with $\Delta_r H^\circ$ determined calorimetrically and $\Delta_r S^\circ$ obtained from the third law of thermodynamics.
3. Statistical thermodynamics (theoretical approach).

Calculation of $\Delta_r G^\circ$ from the standard Gibbs energy of formation ($\Delta_f G^\circ$):

$$\Delta_r G^\circ = \sum_{i=1}^{N_s} v_i \Delta_f G_i^\circ \text{ with } \Delta_f G_i^\circ = \Delta_f H_i^\circ - T \left(\bar{S}_i^\circ + \sum_{j \neq i} v_j \bar{S}_j^\circ \right) \quad (5.321)$$

The entropy summation is over the elements that are required to form compound i . $\Delta_f G_i^\circ$ is the Gibbs energy for formation of species i . Note that at all temperatures $\Delta_f G^\circ(\text{H}^+(aq)) = \Delta_f H^\circ(\text{H}^+(aq)) = \bar{S}^\circ(\text{H}^+(aq)) = 0$.

First use the NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>) to get the enthalpies of formation ($\Delta_f H_i^\circ$) and entropies (S_i°) and finally calculate $\Delta_r G_i^\circ$ by using Eq. (5.321).

Note: Even when $\Delta_r H^\circ$ is positive (i.e., endothermic reaction), $\Delta_r S^\circ$ may be sufficiently large so that it overall produces negative Gibbs energy. Such reactions are entropy driven.

Example. Calculate the standard Gibbs energy of formation for gaseous water $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{H}_2\text{O}(g)$ given the following calorimetric data ($T = 298.15 \text{ K}$):

	$\Delta_f H^\circ$ (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
$\text{H}_2\text{O}(g)$	-241.8	188.8
$\text{H}_2(g)$	0	130.7
$\text{O}_2(g)$	0	205.1

Solution. Apply Eq. (5.321):

$$\Delta_f G^\circ(\text{H}_2\text{O}) = \Delta_f H^\circ(\text{H}_2\text{O}(g)) - T\Delta_f S^\circ(\text{H}_2\text{O}(g)) = \Delta_f H^\circ(\text{H}_2\text{O}(g))$$

$$-T \left\{ \bar{S}_{\text{H}_2\text{O}}^\circ - \underbrace{\bar{S}_{\text{H}_2}^\circ - \frac{1}{2}\bar{S}_{\text{O}_2}^\circ}_{=\sum v_j S_j^\circ} \right\} = (-241.8 \text{ kJ mol}^{-1}) - (298.15 \text{ K})$$

$$\times \{ (0.1888 \text{ kJ K}^{-1} \text{ mol}^{-1}) - (0.1307 \text{ kJ K}^{-1} \text{ mol}^{-1}) - 0.5 (0.2051 \text{ kJ K}^{-1} \text{ mol}^{-1}) \}$$

$$= -228.6 \text{ kJ mol}^{-1}$$

Note that the quantities with Δ_f above are already per mole quantities and therefore do not require use of overbars.

Example. Calculate the equilibrium constants for the following reactions at the indicated temperature:

a) $3\text{O}_2(g) = 2\text{O}_3(g)$ at 25°C

b) $\text{CO}(g) + 2\text{H}_2(g) = \text{CH}_3\text{OH}(g)$ at 500 K ($\Delta_f G^\circ(\text{CH}_3\text{OH}) = -134.3\text{ kJ mol}^{-1}$)

Solution. (a) First we have to calculate $\Delta_f G^\circ$ using the values of $\Delta_f H^\circ = 142.7\text{ kJ mol}^{-1}$ and $\Delta_f S^\circ = \bar{S}_{\text{O}_3}^\circ - \frac{3}{2}\bar{S}_{\text{O}_2}^\circ = -68.8\text{ J K}^{-1}\text{ mol}^{-1}$, which give $\Delta_f G^\circ(\text{O}_3(g)) = \Delta_f H^\circ(\text{O}_3(g)) - T\Delta_f S^\circ(\text{O}_3(g)) = 163.2\text{ kJ mol}^{-1}$ (numerical values from the Chemistry WebBook). Note that the formation reaction for ozone is $\frac{3}{2}\text{O}_2(g) \rightarrow \text{O}_3(g)$.

Then we use Eq. (5.321) to get $\Delta_r G^\circ$ (note that $\Delta_f G^\circ(\text{O}_2(g)) = 0$):

$$\Delta_r G^\circ = 2\Delta_f G^\circ(\text{O}_3(g)) - 3\Delta_f G^\circ(\text{O}_2(g)) = 326.4\text{ kJ mol}^{-1}$$

Next apply Eq. (5.302) to get K :

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = 6.62 \times 10^{-58}$$

(b) First we have to calculate $\Delta_f G^\circ(\text{CO}(g))$ at 500 K temperature. The formation reaction for $\text{CO}(g)$ is: $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g)$. The required values can be found from the Chemistry WebBook but note that the required values must be at 500 K . For example, for CO at 500 K we get (graphite \bar{S}° assumed to be temperature independent):

$$\bar{S}_{\text{CO}(g)}^\circ = 212.8\text{ J mol}^{-1}\text{ K}^{-1}, \bar{S}_{\text{graphite}}^\circ = 5.6\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\bar{S}_{\text{O}_2(g)}^\circ = 220.8\text{ J K}^{-1}\text{ mol}^{-1}, \Delta_f S^\circ(\text{CO}(g)) = \left(212.8 - 5.6 - \frac{1}{2} \times 220.8\right) \frac{\text{J}}{\text{K mol}}$$

$$= 96.8\text{ J K}^{-1}\text{ mol}^{-1} \text{ at } 500\text{ K}$$

The enthalpy at 500 K is $\Delta_f H^\circ(\text{CO}(g)) = -104.6\text{ kJ mol}^{-1}$, which results in $\Delta_f G^\circ(\text{CO}(g)) = -153.0\text{ kJ mol}^{-1}$. For CH_3OH $\Delta_f G^\circ$ at 500 K was given (this could have been calculated using the heat capacity data given in the Chemistry WebBook data). Now Eqs. (5.321) and (5.302) give:

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{CH}_3\text{OH}(g)) - \underbrace{2\Delta_f G^\circ(\text{H}_2(g))}_{=0} - \Delta_f G^\circ(\text{CO}(g))$$

$$= (-134.3\text{ kJ mol}^{-1}) - (-153.0\text{ kJ mol}^{-1}) = 18.7\text{ kJ mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(-\frac{18700\text{ J mol}^{-1}}{(8.31\text{ J K}^{-1}\text{ mol}^{-1})(500\text{ K})}\right) = 1.11 \times 10^{-2}$$

5.5 Effect of temperature on the equilibrium constant 231

The effect of temperature on chemical equilibrium is determined by $\Delta_r H^\circ$:

$$\Delta_r H^\circ \underbrace{=}_{\text{Eq. (4.242)}} -T^2 \left[\frac{\partial (\Delta_r G^\circ / T)}{\partial T} \right]_P \underbrace{=}_{\text{Eq. (5.302)}} RT^2 \left[\frac{\partial (\ln(K))}{\partial T} \right]_P \quad (5.322)$$

$$\Rightarrow \left(\frac{\partial (\ln(K))}{\partial T} \right)_P = \frac{\Delta_r H^\circ}{RT^2} \quad (\text{van't Hoff equation}) \quad (5.323)$$

For endothermic reactions the equilibrium constant increases as the temperature is increased, but for an exothermic reactions the equilibrium constant decreases as the temperature is increased. This means that endothermic (“requires heat”) reactions are favored at higher temperature whereas exothermic (“releases heat”) are favored at lower temperatures. The equilibrium shifts in direction where the reaction can “consume” more heat.

If $\Delta_r H^\circ$ is independent of temperature, integration of Eq. (5.323) from T_1 to T_2 gives:

$$\ln \left(\frac{K(T_2)}{K(T_1)} \right) = \frac{\Delta_r H^\circ (T_2 - T_1)}{RT_1 T_2} \quad (5.324)$$

where $K(T_1)$ and $K(T_2)$ are the equilibrium constants at T_1 and T_2 , respectively.

232

Note: If $\Delta_r H^\circ$ is independent of temperature, then $\Delta_r C_P^\circ$ is zero (Eqs. (2.112) and (2.140)). It will turn out later in Eq. (5.330) that since $\Delta_r C_P^\circ$ is zero then $\Delta_r S^\circ$ is also independent of temperature.

By assuming $\Delta_r C_P^\circ = 0$ and combining Eqs. (5.302) and (5.304) we get:

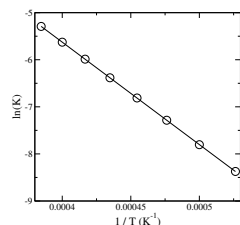
$$\begin{aligned} \Delta_r G^\circ &= -RT \ln(K) \quad \text{and} \quad \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \\ \Rightarrow \ln(K) &= -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \end{aligned} \quad (5.325)$$

Because $\Delta_r H^\circ$ and $\Delta_r S^\circ$ were assumed to be independent of temperature, plotting this function should yield a straight line ($\ln(K)$ vs. $1/T$).

Example. Calculate $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for the reaction: $\text{N}_2(g) + \text{O}_2(g) = 2\text{NO}(g)$. Assume that $\Delta_r C_P^\circ$ is zero. The following values for K were obtained experimentally:

T (K)	1900	2000	2100	2200	2300	2400	2500	2600
K ($\times 10^{-4}$)	2.31	4.08	6.86	11.0	16.9	25.1	36.0	50.3

Solution. Use Eq. (5.325) to obtain the slope and the intercept from a $\ln(K)$ vs. $1/T$ plot. This must be done by fitting Eq. (5.325) to the experimental data. From the slope one can obtain $\Delta_r H^\circ$ by multiplying by $-R$ and $\Delta_r S^\circ$ by multiplying the intercept by R . The plot (data and fitting) is shown below.



$$\begin{aligned}\text{Slope} &= -\Delta_r H^\circ / R = -21.8 \times 10^3 \text{ K} \\ \text{Intercept} &= \Delta_r S^\circ / R = 3.08\end{aligned}$$

The values for $\Delta_r H^\circ$ and $\Delta_r S^\circ$ can be now calculated:

$$\begin{aligned}\Delta_r H^\circ &= -\text{slope} \times R = -(-21.9 \times 10^3 \text{ K}) \times (8.315 \text{ J K}^{-1} \text{ mol}^{-1}) = 182 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ &= \text{intercept} \times R = (3.08) \times (8.315 \text{ J K}^{-1} \text{ mol}^{-1}) = 25.6 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Note that the assumption of no temperature dependency in $\Delta_r H^\circ$ and $\Delta_r S^\circ$ appears to be a good one here. If this was not the case, the above plot would not yield a straight line (because “the slope and intercept would depend on T ”).

The standard reaction entropy $\Delta_r S^\circ$ indicates how much the entropy changes in a reaction under standard conditions and at a given temperature. For a given reaction it can be calculated by:

$$\Delta_r S^\circ = \sum_{i=1}^{N_s} v_i \bar{S}_i^\circ \quad (5.326)$$

Example. Calculate the standard reaction entropies for the following reactions at 298 K by using the data in the Chemistry WebBook:

- (a) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) = \text{H}_2\text{O}(g)$
- (b) $\text{N}_2(g) + 3\text{H}_2(g) = 2\text{NH}_3(g)$

Solution. Eq. (5.326) gives the following results:

$$\begin{aligned}\text{(a)} \quad \Delta_r S^\circ &= \bar{S}_{\text{H}_2\text{O}(g)}^\circ - \bar{S}_{\text{H}_2(g)}^\circ - \frac{1}{2}\bar{S}_{\text{O}_2(g)}^\circ = (69.95 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - (130.68 \text{ J K}^{-1} \text{ mol}^{-1}) - \frac{1}{2}(205.15 \text{ J K}^{-1} \text{ mol}^{-1}) = -163.33 \text{ J K}^{-1} \text{ mol}^{-1} \\ \text{(b)} \quad \Delta_r S^\circ &= 2\bar{S}_{\text{NH}_3(g)}^\circ - \bar{S}_{\text{N}_2(g)}^\circ - 3\bar{S}_{\text{H}_2(g)}^\circ = 2(192.77 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - (191.61 \text{ J K}^{-1} \text{ mol}^{-1}) - 3(130.68 \text{ J K}^{-1} \text{ mol}^{-1}) = -198.11 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

In general, both $\Delta_r H^\circ$ and $\Delta_r S^\circ$ depend on temperature because the reaction heat capacity depends on temperature. In Eqs. like (2.141) and (3.191) we have already seen this kind of temperature dependency (note that Δ_r and Δ_f quantities are very similar - one is for some given reaction and the other is for a formation reaction and thus they behave exactly the same way). To summarize the results:

$$\Delta_f H_i^\circ(T) = \Delta_f H_i^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T \bar{C}_{P,i}^\circ(T') dT' \quad (5.327)$$

$$\bar{S}_i^\circ(T) = \bar{S}_i^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T \frac{\bar{C}_{P,i}^\circ(T')}{T'} dT' \quad (5.328)$$

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T \Delta_r C_P^\circ(T') dT' \quad (5.329)$$

$$\Delta_r S^\circ(T) = \Delta_r S^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T \frac{\Delta_r C_P^\circ(T')}{T'} dT' \quad (5.330)$$

Remember also Eq. (2.139): $\Delta_r H^\circ = \sum_{i=1}^{N_s} v_i \Delta_f H_i^\circ$ and $\Delta_r S^\circ = \sum_{i=1}^{N_s} v_i \Delta_f S_i^\circ$. Recall also that $C_{P,i}^\circ$ can be represented as power series in T .

The above results together with $\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T \Delta_r S^\circ(T)$ can be used for deriving an expression for $\Delta_r G^\circ$:

$$\Delta_r G^\circ(T) = \Delta_r G^\circ(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T \Delta_r C_P^\circ(T') dT' - T \int_{298.15 \text{ K}}^T \frac{\Delta_r C_P^\circ(T')}{T'} dT' \quad (5.331)$$

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺ ↻

Note that above $\Delta_r G^\circ(298.15 \text{ K})$ must be interpreted as $(T \neq 298.15 \text{ K})$:

$$\Delta_r G^\circ(298.15 \text{ K}) = \Delta_r H^\circ(298.15 \text{ K}) - T \Delta_r S^\circ(298.15 \text{ K})$$

Recall from Eq. (5.302) that $\ln(K) = -\Delta_r G^\circ/RT$ and thus we get:

$$\ln(K(T)) = \frac{298.15 \text{ K}}{T} \times \ln(K(298.15 \text{ K})) - \frac{1}{RT} \int_{298.15 \text{ K}}^T \Delta_r C_P^\circ(T') dT' \quad (5.332)$$

$$+ \frac{1}{R} \int_{298.15 \text{ K}}^T \frac{\Delta_r C_P^\circ(T')}{T'} dT'$$

However, calculation of the temperature dependency in K is rather tedious this way. Numerical integration methods are a great help (i.e. using computers). Another way is to integrate the Gibbs-Helmholtz Eq. (4.241). Also note that Eq. (5.332) can be simplified if the reaction heat capacities are assumed to be independent of temperature.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺ ↻

5.6 Effect of pressure, initial composition, and inert gases on the equilibrium composition

The effect of pressure

Consider a mixture of ideal gases where the partial pressure of is gas component i can be written in terms of the molar fraction y_i and the total pressure P : $P_i = y_i P$. Inserting this into Eq. (5.307) we get:

$$K = \prod_{i=1}^{N_s} \left(\frac{P_i}{P^\circ} \right)^{v_i} = \prod_{i=1}^{N_s} \left(\frac{y_i P}{P^\circ} \right)^{v_i} = \prod_{i=1}^{N_s} \left(\frac{P}{P^\circ} \right)^{v_i} \prod_{i=1}^{N_s} y_i^{v_i} \quad (5.333)$$

$$= \left(\frac{P}{P^\circ} \right)^v K_y \text{ where } v = \sum_{i=1}^{N_s} v_i \text{ and } K_y = \prod_{i=1}^{N_s} y_i^{v_i}$$

Note that K_y depends on the molar fractions of the gas components and changes in it imply changes in the molar fractions of the different components. Now consider changes in the total pressure P at constant temperature and rewrite the previous equation as:

$$K_y = \left(\frac{P}{P^\circ} \right)^{-v} K \quad (5.334)$$

Consider the following three cases:

1. $v < 0$: The total amount of moles of gas decreases in the reaction. According to Eq. (5.334) K_y should increase as pressure increases. This means that the products are favored over the reactants (i.e. balance shifts forward).
2. $v > 0$: The total amount of moles of gas increases in the reaction. According to Eq. (5.334) K_y should decrease as pressure increases. This means that the reactants are favored over the products (i.e. balance shifts backward).
3. $v = 0$: The total amount of moles of gas remains independent of pressure. Thus changes in pressure do not change the molar fractions of the gases.

Notes:

1. This result reflects the Le Chatelier's principle.
2. If the reactants and products are solids or liquids, the effect of pressure on the equilibrium is small.

The effect of initial composition on equilibrium

First we write the molar fraction y_i in terms of the extent of reaction ξ . The amount of species i and the total amount of gas for a given ξ are given by:

$$n_i(\xi) = n_{i,0} + v_i \xi \text{ and } n_{tot}(\xi) = n_{tot,0} + v \xi$$

From these quantities y_i can be calculated: $y_i(\xi) = \frac{n_i(\xi)}{n_{tot}(\xi)} = \frac{n_{i,0} + v_i \xi}{n_{tot,0} + v \xi}$

Inserting this into definition of K_y we get the following relation between K_y and ξ :

$$K_y = \prod_{i=1}^{N_s} y_i^{v_i} = \prod_{i=1}^{N_s} \left(\frac{n_{i,0} + v_i \xi}{n_{tot,0} + v \xi} \right)^{v_i} = \left(\frac{1}{n_{tot,0} + v \xi} \right)^v \times \prod_{i=1}^{N_s} (n_{i,0} + v_i \xi)^{v_i} \quad (5.335)$$

By combining Eqs. (5.333) and (5.335), the equilibrium constant can be written as:

$$K = \left(\frac{P/P^\circ}{n_{tot,0} + v \xi} \right)^v \times \prod_{i=1}^{N_s} (n_{i,0} + v_i \xi)^{v_i} \quad (5.336)$$

1. Consider addition of inert gas (i.e. one that does not take part in chemical reaction) with temperature and volume constant. Remember that since the amount of substance is not constant, we have four variables (P , V , T , and n) to consider. The amount of inert gas added is denoted by n_{inert} . The total amount of gas is now given by $n_{tot,0} + v \xi + n_{inert}$ and note that the inert component cancels out from the product on the right in the equation above because it remains identical on both sides of the chemical equation. The above equation now takes the following form:

$$K = \left(\frac{P/P^\circ}{n_{tot,0} + v \xi + n_{inert}} \right)^v \prod_{i=1}^{N_s} (n_{i,0} + v_i \xi)^{v_i} \quad (5.337)$$

As temperature and volume are constants, it is instructive to rewrite Eq. (5.337) in terms of these variables by using the ideal gas law:

$$\begin{aligned} K &= \left(\frac{\left((n_{tot,0} + v \xi + n_{inert}) \frac{RT}{V} \right) / P^\circ}{n_{tot,0} + v \xi + n_{inert}} \right)^v \prod_{i=1}^{N_s} (n_{i,0} + v_i \xi)^{v_i} \quad (5.338) \\ &= \left(\frac{RT}{VP^\circ} \right)^v \prod_{i=1}^{N_s} (n_{i,0} + v_i \xi)^{v_i} \end{aligned}$$

Note that we had assumed that both T and V were constants, which means that the right hand side above is independent of n_{inert} . Therefore addition of inert gas component to the reactive gas mixture does not change equilibrium if T and V are kept constant during the addition (i.e. only the total pressure changes).

2. Next consider addition of an inert gas with temperature and pressure kept constant (note that V changes in this process). If n_{inert} changes, the prefactor in Eq. (5.337) changes as well. Since $K = K(T)$ and temperature is constant, the product term in Eq. (5.337) (i.e., K_y) must counter balance the change. This means that the mole fractions y_i must take new values (i.e., the composition of the gas mixture changes).

Summary:

$v < 0$: addition of inert gas shifts the balance in chemical equation to the left.
 $v = 0$: addition of inert gas does not change the composition of the gas.
 $v > 0$: addition of inert gas shifts the balance in chemical equation to the right.

5.7 Equilibrium constants for gas reactions written in terms of concentrations

Previously the equilibrium constants were written in terms of pressure. Now the task is to express the equilibrium constant constant in terms of concentrations for gas phase reactions.

K_P = Equilibrium constant calculated using partial pressures.

K_c = Equilibrium constant calculated using concentrations.

Below we will show that usually $K_P \neq K_c$ and derive the relation between them. First we note that partial pressures are related to concentrations c_i by $P_{i,eq} = n_{i,eq}RT/V = c_{i,eq}RT$ and then Eq. (5.307) gives:

$$K_P = \prod_{i=1}^{N_s} \left(\frac{c_i RT}{P^\circ} \right)^{v_i} \quad (5.339)$$

Next we introduce standard concentration denoted by c° , which is 1 mol dm^{-3} and insert this into Eq. (5.339):

$$K_P = \prod_{i=1}^{N_s} \left[\left(\frac{c_i}{c^\circ} \right) \left(\frac{c^\circ RT}{P^\circ} \right) \right]^{v_i} = \left(\frac{c^\circ RT}{P^\circ} \right)^v \prod_{i=1}^{N_s} \left(\frac{c_i}{c^\circ} \right)^{v_i} = \left(\frac{c^\circ RT}{P^\circ} \right)^v K_c \quad (5.340)$$

where $v = \sum_{i=1}^{N_s} v_i$. Also K_c is defined as:

$$K_c = \prod_{i=1}^{N_s} \left(\frac{c_i}{c^\circ} \right)^{v_i} \quad (5.341)$$

Note that K_c is also a function of temperature only (just like K_P).

Example. What is the value of the equilibrium constant K_c for the dissociation of ethane into methyl radicals at 1000 K? The reaction is: $\text{C}_2\text{H}_6(g) = 2\text{CH}_3(g)$. $\Delta_f G^\circ(\text{CH}_3) = 159.8 \text{ kJ mol}^{-1}$ and $\Delta_f G^\circ(\text{C}_2\text{H}_6) = 109.6 \text{ kJ mol}^{-1}$.

Solution. First we calculate $\Delta_r G^\circ$ by Eq. (5.321):

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f G^\circ(\text{CH}_3) - \Delta_f G^\circ(\text{C}_2\text{H}_6) = 2(159.8 \text{ kJ mol}^{-1}) - (109.6 \text{ kJ mol}^{-1}) \\ &= 210.1 \text{ kJ mol}^{-1}\end{aligned}$$

Now Eq. (5.302) gives K_P :

$$K_P = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(\frac{-210.1 \text{ kJ mol}^{-1}}{(8.315 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(10^3 \text{ K})}\right) = 1.062 \times 10^{-11}$$

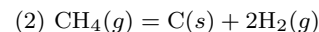
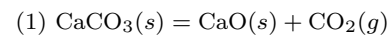
Finally convert from K_P to K_c by Eqs. (5.340) and (5.341):

$$\begin{aligned}K_c &= \frac{([\text{CH}_3]/c^\circ)^2}{[\text{C}_2\text{H}_6]/c^\circ} = K_P \frac{P^\circ}{c^\circ RT} = (1.062 \times 10^{-11}) \\ &\times \frac{1 \text{ bar}}{(1 \text{ mol L}^{-1})(0.08315 \text{ L bar K}^{-1} \text{ mol}^{-1})(1000 \text{ K})} = 1.278 \times 10^{-13}\end{aligned}$$

Note that in above c° is required to get the right unit cancellation for K_c .

5.8 Thermochemistry of heterogeneous reactions

A reaction involving more than one phase that does not involve equilibria of species between phases is referred to as a heterogeneous reaction. For example the following reactions are heterogeneous:



Previously we have seen that pure gas phase reactions do not go to completion essentially because of entropy of mixing. However, depending on the initial conditions, heterogeneous reactions can proceed to completion. This can be seen by writing the equilibrium constant for reactions (1) and (2) above:

$$K_P = \frac{P_{\text{CO}_2}}{P^\circ} \quad (5.342)$$

$$K_P = \frac{P_{\text{H}_2}^2}{P_{\text{CH}_4} P^\circ} \quad (5.343)$$

The reason why solids do not need to be entered above, is that their activities are very close to one up to moderate pressures. As such they do not contribute to the equilibrium constant. Reaction (1) may go all the way to completion whereas reaction (2) may not because there are gaseous products on both sides of the chemical equation. From (5.60) we can distinguish two different cases for reaction (1):

1. The reaction will go to completion trying to satisfy Eq. (5.342) (may not get that far).
2. The reaction will not go to completion and stops when Eq. (5.342) is satisfied.

5.9 Degrees of freedom and phase rule

In this section we will derive the Gibbs phase rule:

$$F = C - p + 2 \quad (5.344)$$

- $F =$ The total number of variables that must be used in specifying the system.
 $C =$ The number of components present in the system (“# of species - # of reactions”: $N_s - R$).
 $p =$ The number of phases present in the system.

Justification:

Consider system with p phases. If a phase contains C components, its composition may be specified by $(C - 1)$ mole fractions (the remaining fraction can be obtained from the fact that their sum must equal to 1). The total number of variables for all the phases is given by $p \times (C - 1)$. In addition to these, one must also specify two more variables (like P & T , V & P or V & T). Thus up to this point we can conclude that we at least have $F = p \times (C - 1) + 2$. Next we consider phase equilibria between p different phases. For phases $\alpha, \beta, \gamma, \dots$ we must have at equilibrium $\mu_{\alpha,i} = \mu_{\beta,i} = \mu_{\gamma,i} = \dots$ for each component i . Thus there are $(p - 1)$ such relationships for each component, which reduces the total number of required variables by $C(p - 1)$.

Finally, by summing the previous contributions, we get the Gibbs phase rule:

$$F = [p(C - 1) + 2] - C(p - 1) = C - p + 2$$

Example. The reaction $\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g)$ is at equilibrium.

- (a) How many degrees of freedom are there when all three compounds are present at equilibrium?
 (b) How many degrees of freedom are there when only $\text{CaCO}_3(s)$ and $\text{CO}_2(g)$ are present?

Solution.

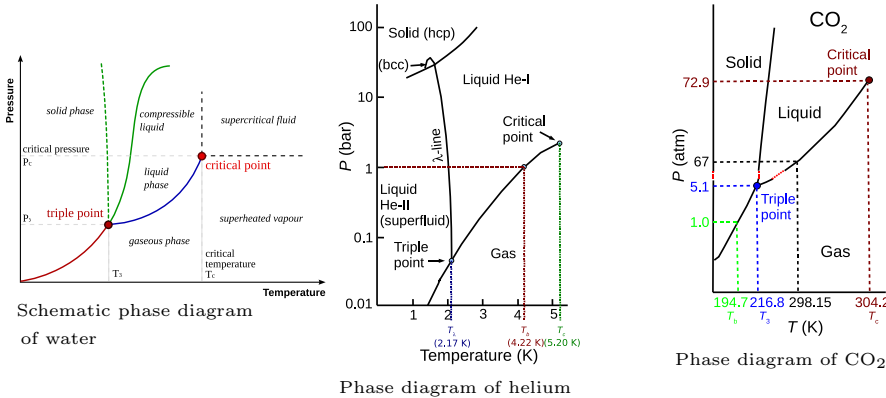
- (a) The number of components: $C = N_s - R = 3 - 1 = 2$. Three compounds and one chemical reaction.
 The number of phases: $p = 2$ (solid and gas).
 The total number of variables needed: $F = C - p + 2 = 2$.
 Thus both temperature and pressure may be varied independently without destroying a phase.
- (b) $C = N_s - R = 2 - 0 = 2$ (no reaction; $R = 0$).
 $p = 2$ (solid & gas).
 $F = 2 - 2 + 2 = 2$. This is the same as in a) because the restriction due to chemical reaction was removed but there is one component less. Both temperature and pressure may be varied without destroying a phase.

Chapter 6: Phase equilibrium

“At constant temperature and pressure chemical potentials can be used to understand stability of different phases.”

6.1 Phase diagrams of one-component systems

Earlier we saw that plotting a $P - V - T$ surface in three dimensions is difficult. Furthermore we have seen (i.e., the Gibbs phase rule) that at maximum two variables are need to defined for describing a one-component system. Most commonly P and T are chosen as variables when phase-diagrams are plotted.



Note that along the phase boundary lines two phases exist in equilibrium. The Gibbs phase rule now gives $F = 1$, which means that only one variable may be specified independently. The boundary lines can be understood as functions and as such they introduce a dependency between P and T (i.e. reduces F to 1). At points where all three different phases exist at the same time (“triple point”) we have $F = 0$ (i.e. they are just points in the graphs and both P and T are fixed).

What defines the phase boundaries?

Recall that at constant T and P the the equilibrium (i.e. $dG = 0$) between two phases α and β is Eq. (4.259):

$$dG = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta = \mu_\alpha dn - \mu_\beta dn = 0 \Rightarrow \mu_\alpha = \mu_\beta$$

In order to tell which phase is stable at given pressure and temperature, we must calculate the chemical potentials for each phase and compare them. The phase with the lowest chemical potential is stable. To obtain general statements about stabilities of different phases, we must recall the following results (Eqs. (4.260) and (4.261)):

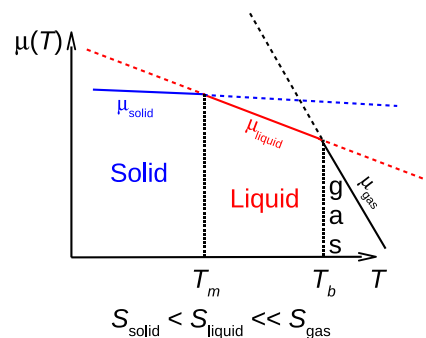
$$-\bar{S} = \left(\frac{\partial \mu}{\partial T} \right)_P \quad (6.345)$$

$$\bar{V} = \left(\frac{\partial \mu}{\partial P} \right)_T \quad (6.346)$$

Remember that derivatives define slopes (here for the chemical potential μ).

1. Dependency of μ on temperature

We will use Eq (6.345) above to predict the slopes for $\mu = \mu(T)$. Remember that S is always non-negative, which means that $\mu(T)$ must have a non-negative slope. From our statistical interpretation of entropy can conclude that: $\bar{S}(\text{solid}) < \bar{S}(\text{liquid}) < \bar{S}(\text{gas})$. Based on these results we can graph $\mu(T)$ for each phase qualitatively.



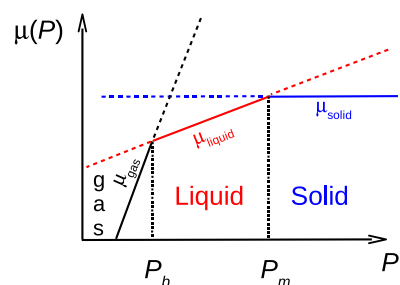
The slopes of the lines are given by $-\bar{S}_{\text{solid}}$, $-\bar{S}_{\text{liquid}}$ and $-\bar{S}_{\text{gas}}$.

Note that the entropy only gives the slope. Also this approximation assumes that $\mu(T)$ is a straight line.

T_m = melting temperature
 T_b = boiling temperature
 P = constant

2. Dependency of μ on pressure

The previous Eq. (6.346) gives the slope for $\mu(P)$ when temperature is constant. The slope is equal to the molar volume, which is a non-negative quantity. The molar volumes for different phases are known to follow: $\bar{V}_{\text{solid}} < \bar{V}_{\text{liquid}} \ll \bar{V}_{\text{gas}}$. An exception to this rule is, for example, water, which we will consider separately.



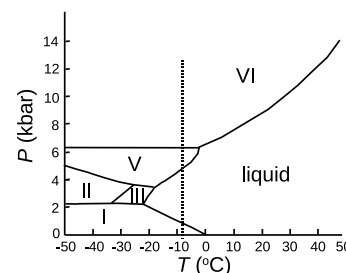
The slopes of the lines are given by the molar volumes for the different phases. Note that the molar volume only gives the slope. Also this approximation assumes that $\mu(P)$ is a straight line.

P_m = melting pressure
 P_b = boiling pressure
 T = constant

If gas is compressed, it will first become liquid and upon more compression it will eventually become a solid. At some given temperature a liquid can be made to boil if the pressure is reduced accordingly. For example, vacuum distillation is based on this principle.

For water we have: $\bar{V}_{\text{liquid}} < \bar{V}_{\text{solid}} \ll \bar{V}_{\text{gas}}$

Here it turns out that the volume of the solid is larger than the liquid (the density of liquid is higher than the solid). For this reason, for example, ice cubes stay on top of water or water upon freezing expands and in nature this expansion process can break even rocks. Most solids sink in the corresponding liquid because they contract on freezing (i.e., the density increases).

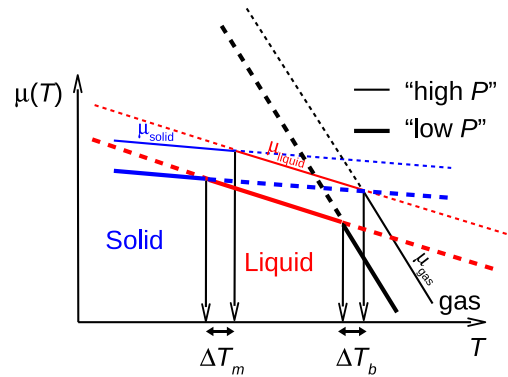


The numbers in the graph refer to different solid crystal structures of water (i.e., ice). If the temperature is fixed at the dashed line and the initial pressure is zero then upon increasing the pressure we will observe the following phases: solid(I), liquid, solid(V) and finally solid(IV).

Other substances that expand when they freeze are: sulfuric acid, gallium, acetic acid and silicon. For chemists this information is very useful in practical laboratory work: if you freeze these materials in “fragile” containers, you may break the container! The term fragility here refers to the ability of the container to withstand expansion (e.g., quartz vs. normal glass).

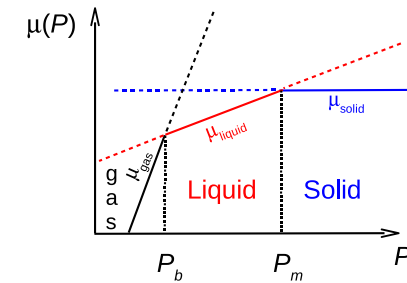
3. Combined effect of pressure and temperature

The combined effect of pressure and temperature is shown below by plotting $\mu(T)$ vs. T at two different pressures (“high” and “low”):



Note the shift in T_m and T_b as a function of pressure. At higher P both T_m and T_b increase.

The previously discussed changes in phase are said to be first order phase transitions. The first order refers to the fact the the chemical potential has discontinuous first derivative with respect to pressure and temperature. For example $d\mu(P)/dP$ is discontinuous at phase transitions:

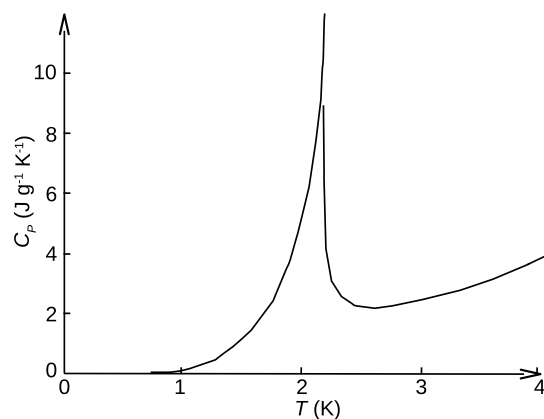


Thus above on each side of the non-differentiable points, the substance has different molar volumes. At transition points heat capacities also tend to approach infinity. This can be understood qualitatively by inspecting Eqs. (2.100) and (2.112):

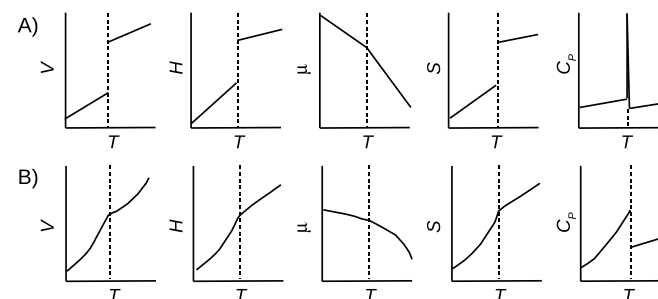
$$C_V = \frac{dq_V}{dT} \text{ and } C_P = \frac{dq_P}{dT} \Rightarrow \Delta T = \frac{q_V}{C_V(T)} \text{ and } \Delta T = \frac{q_P}{C_P(T)}$$

At transition points all the supplied heat (q) is used for driving the phase transition (i.e. the temperature remains constant until the phase transition is complete). According to the previous equations this can only happen if the heat capacities are infinite at the transition points ($\Delta T = 0, q > 0 \Rightarrow C \rightarrow \infty$).

Example. A special case of phase transition occurs between two liquid phases He-I and He-II (normal and superfluid ^4He) at low temperatures. Due to the shape of the transition, it is also called λ -transition (under saturated vapor pressure this occurs at 2.17 K).



In a second order phase transition (no heat involved in transition) the first derivative of chemical potential is continuous but the second derivative has a discontinuity. The heat capacity does not become infinite at these points but show only a discontinuous jump. Behavior of various thermodynamic quantities at first and second order transition points is shown below.



A) First order phase transition, B) Second order phase transition

Examples of 2nd order phase transitions are ferromagnetic, superconductor and superfluid transitions. The classification scheme for phase transitions was proposed by Paul Ehrenfest (1880 - 1933). Formally his classification is not quite correct and one should differentiate between the 1st and 2nd order phase transitions by the involvement of heat exchange.

6.2 The Clapeyron equation

Consider a one-component system with two phases. The Gibbs phase rule is now: $F = C - p + 2 = 1$. At equilibrium the chemical potentials (i.e. the Gibbs energy energy at constant P and T) for both phases (denoted by α and β) must be equal (see Eq. (4.259)):

$$\mu_\alpha = \mu_\beta \quad (6.347)$$



Benoit Clapeyron,
French engineer
and physicist
(1799 - 1864).

If either P or T is changed one of the phases α or β will disappear. However, it is possible to vary both P and T in such a way that both phases will remain (i.e. to follow the phase boundary line in a phase diagram; phase boundary line = phase coexistence curve).

If derivative dP/dT was known along the phase coexistence curve, it would be possible to calculate, for example, how P must be changed if T is changed by certain amount while preserving both phases. It turns out that this derivative is given by the Clapeyron equation.

Clapeyron equation:

The phase equilibrium relation Eq. (6.347) must hold for any P and T along the phase coexistence line. If the pressure and temperature are varied with the restriction $\mu_\alpha = \mu_\beta$, we can also write $d\mu_\alpha = d\mu_\beta$.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺

The Gibbs-Duhem equation (Eq. (4.272)) for both phases gives:

$$n_\alpha d\mu_\alpha - V_\alpha dP + S_\alpha dT = 0$$

$$n_\beta d\mu_\beta - V_\beta dP + S_\beta dT = 0$$

Solving for $d\mu$'s gives:

$$d\mu_\alpha = \bar{V}_\alpha dP - \bar{S}_\alpha dT$$

$$d\mu_\beta = \bar{V}_\beta dP - \bar{S}_\beta dT$$

Since $d\mu_\alpha = d\mu_\beta$, we get essentially the Clapeyron equation:

$$\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT \quad (6.348)$$

This can be rewritten (using Eq. (3.176); $\Delta S = \Delta H/T$) as:

$$\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{\Delta \bar{H}}{T \Delta \bar{V}} \quad (6.349)$$

The deltas in this equation refer to differences in the values for the two phases. This Clapeyron equation may be applied to vaporization, sublimation, fusion or the transition between two solid phases of a pure substance.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺

Example. What is the rate of change per Pascal (Pa) in the boiling point of water at a 100 °C in atmospheric pressure? The molar enthalpy of vaporization is 40.69 kJ mol⁻¹, the molar volume of liquid water is 0.019 × 10⁻³ m³ mol⁻¹, and the molar volume of steam is 30.199 × 10⁻³ m³ mol⁻¹. All values are given at 100 °C and 1.01325 bar.

Solution. Use the Clapeyron Eq. (6.349):

$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{T(\bar{V}_g - \bar{V}_l)} = \frac{40690 \text{ J mol}^{-1}}{(373.15 \text{ K})(30.180 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})} = 3613 \text{ Pa K}^{-1}$$

Finally use the reciprocal identity to obtain the rate:

$$\frac{dT}{dP} = \left(\frac{dP}{dT}\right)^{-1} = \frac{1}{3613 \text{ Pa K}^{-1}} = 2.76 \times 10^{-4} \text{ K Pa}^{-1}$$

Example. Calculate the change in pressure required to increase the freezing point of water by 1 mK. At 273.15 K the heat of fusion of ice is 333.5 J g⁻¹, the density of water is 0.9998 g cm⁻³ (= g / mL = kg / L), and the density of ice is 0.9168 g cm⁻³.

Solution. First we note that the molar volumes are given by the inverse of density:

$$\bar{V} = \frac{1}{\rho}$$

Therefore we get the molar volumes for the liquid and solid:

$$\bar{V}_l = \frac{1}{0.9998 \text{ g cm}^{-3}} = 1.0002 \text{ cm}^3 \text{ g}^{-1} \text{ and } \bar{V}_s = \frac{1}{0.9168 \text{ g cm}^{-3}} = 1.0908 \text{ cm}^3 \text{ g}^{-1}$$

Note that we have expressed everything in terms of grams rather than moles. If molar volume would be needed in units of volume / mol then one should use the molecular weight of the substance to convert. Provided that the molar quantities of ΔH and ΔV are independent of temperature and pressure, we can integrate Eq. (6.349):

$$\begin{aligned} dP &= \frac{\Delta_{fus}\bar{H}}{T\Delta\bar{V}}dT \Rightarrow \Delta P = \frac{\Delta_{fus}\bar{H}}{\Delta\bar{V}} \int_{T_i}^{T_f} \frac{dT}{T} = \frac{\Delta_{fus}\bar{H}}{\Delta\bar{V}} \ln\left(\frac{T_f}{T_i}\right) \\ &\approx \frac{\Delta_{fus}\bar{H}}{\Delta\bar{V}} \left(\frac{T_f}{T_i} - 1\right) \approx \frac{\Delta_{fus}\bar{H}}{\Delta\bar{V}T_i} \times \Delta T \end{aligned}$$

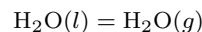
For a change of 1 mK both $\Delta_{fus}H$ and the molar volumes are approximately constant. In the present case $T_i = 273.150 \text{ K}$ (freezing point of water at ambient pressure), $\Delta T = 0.001 \text{ K}$ and $T_f = 273.151 \text{ K}$. The task is now to find ΔP :

$$\Delta P = \frac{(333.5 \text{ J g}^{-1})(0.001 \text{ K})}{(-9.06 \times 10^{-8} \text{ m}^3 \text{ g}^{-1})(273.15 \text{ K})} = -1.348 \times 10^4 \text{ Pa} = -0.134 \text{ bar}$$

Note that for water $dP/dT < 0$! This means that the phase boundary slope in the phase diagram is negative. In most cases $\bar{V} > 0$ and $dP/dT > 0$.

Example. Calculate the vapor pressure of $\text{H}_2\text{O}(l)$ at 298.15 K when the following values are given: $\Delta_f G_{298\text{ K}}^\circ(\text{H}_2\text{O}(g)) = -228.6\text{ kJ mol}^{-1}$ and $\Delta_f G_{298\text{ K}}^\circ(\text{H}_2\text{O}(l)) = -237.1\text{ kJ mol}^{-1}$. Assume that the gases follow the ideal gas law.

Solution. Phase changes can be considered as “chemical reactions”:



Recall Eq. (5.302) and the definition of equilibrium constant Eq. (5.301):

$$\Delta_r G^\circ = -RT \ln(K) = -RT \ln \left(\underbrace{\frac{a(\text{H}_2\text{O}(g))}{a(\text{H}_2\text{O}(l))}}_{=1} \right) = -RT \ln(a(\text{H}_2\text{O}(g)))$$

To get $\Delta_r G^\circ$ we use Eq. (5.321):

$$\begin{aligned} \Delta_r G^\circ &= \Delta_f G^\circ(\text{H}_2\text{O}(g)) - \Delta_f G^\circ(\text{H}_2\text{O}(l)) = (-228.6\text{ kJ mol}^{-1}) - (-237.1\text{ kJ mol}^{-1}) \\ &= 8.56\text{ kJ mol}^{-1} \end{aligned}$$

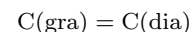
The ideal gas assumption with Eq. (5.301) and replacing the subscript r with vap (our “reaction” is vaporization):

$$\Delta_{vap} G^\circ = -RT \ln(P_{\text{H}_2\text{O}(g)}/P^\circ) \Rightarrow P_{\text{H}_2\text{O}(g)} = P^\circ \exp\left(-\frac{\Delta_{vap} G^\circ}{RT}\right)$$

$$P_{\text{H}_2\text{O}(g)} = (1\text{ bar}) \exp\left(-\frac{8560\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})}\right) = 0.032\text{ bar}$$

Example. Calculate the equilibrium pressure for the conversion of graphite to diamond at 25 °C. The densities of graphite and diamond may be taken to be 2.25 and 3.51 g cm⁻³, respectively, independent of pressure, in calculating the change of ΔG with pressure.

Solution. Consider equilibrium reaction:



where $\Delta_r G^\circ = \Delta_f G^\circ(\text{dia}) - \Delta_f G^\circ(\text{gra}) = (2900 - 0)\text{ J/mol}$. Eq. (4.222) can now be applied: $\Delta\bar{V} = \left(\frac{\partial(\Delta_r G)}{\partial P}\right)_{T,n}$. This can be integrated:

$$\int_{\Delta_r G^\circ}^{\Delta_r G} d(\Delta_r G) = \int_{P^\circ}^P \Delta\bar{V} dP$$

where $\Delta\bar{V} = \bar{V}(\text{dia}) - \bar{V}(\text{gra})$. Integration of this equation leads to ($\Delta P = P - P^\circ$):

$$\Delta_r G = \Delta_r G^\circ + \Delta\bar{V} \Delta P$$

where $\Delta_r G = 0$ at equilibrium. Solving for ΔP gives:

$$\Delta P = \frac{\Delta_r G - \Delta_r G^\circ}{\Delta \bar{V}} = \frac{-2900 \text{ kJ/mol}}{-1.91 \times 10^{-6} \text{ m}^3/\text{mol}} = 1.52 \times 10^9 \text{ Pa}$$

and the change in molar volume is obtained from:

$$\bar{V} = (12 \text{ g mol}^{-1}) \left(\frac{1}{3.51 \text{ g m}^{-3}} - \frac{1}{2.25 \text{ g m}^{-3}} \right) \times 10^{-6} = -1.91 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

The required pressure is $P = P^0 + \Delta P \approx 1.52 \times 10^9 \text{ Pa}$. Since the temperature was fixed at 25 °C, this much pressure must be applied in order to reach the two-phase equilibrium (i.e., must be located on the phase boundary line).

6.3 The Clausius-Clapeyron equation

For vaporization and sublimation processes Rudolph Clausius showed that the Clapeyron equation may be simplified by assuming that the vapor phase obeys the ideal gas law and the molar volume of the liquid (\bar{V}_l) is small in comparison with the molar volume of the gas (\bar{V}_g). Substituting RT/P for \bar{V}_g , Eq. (6.349) becomes:

$$\frac{dP}{dT} \approx \frac{\Delta_{vap}H}{T\bar{V}_g} = \frac{P\Delta_{vap}H}{RT^2} \quad (6.350)$$

By separating variables to the opposite sides of the equation, Eq. (6.350) becomes:

$$\frac{dP}{P} = \frac{\Delta_{vap}H}{RT^2} dT \Rightarrow \int_{P^\circ}^P \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta_{vap}H}{RT^2} dT \quad (6.351)$$

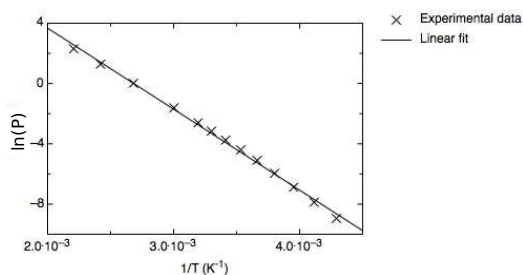
If $\Delta_{vap}H$ is assumed to be independent of temperature, we get:

$$\ln \left(\frac{P}{P^\circ} \right) = \frac{\Delta_{vap}H}{R} \int_{T_1}^{T_2} T^{-2} dT = \frac{\Delta_{vap}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6.352)$$

This can also be written as (indefinite integral):

$$\ln(P) = -\frac{\Delta_{vap}H}{RT} + C \text{ where } C \text{ is a constant} \quad (6.353)$$

This shows that a plot of $\ln(P)$ vs. $1/T$ should be a straight line. When P and T are obtained from experiments, it is possible to extract $\Delta_{vap}H^\circ$ from the (P, T) data. Such data is shown for water as an example below.



A linear fit gives $\Delta_{vap}H^\circ = 44.7 \text{ kJ mol}^{-1}$ (literature value 44.0 kJ mol^{-1} at 298 K). Note that the above experiment gives an average value for this quantity over the measurement temperature range as there is a small dependency on temperature.

The Clausius-Clayperon equation can also be written as:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap}H(T_2 - T_1)}{RT_1T_2} = \frac{\Delta_{vap}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (6.354)$$

The above derivations suffer from two approximations: 1) $\Delta_{vap}H^\circ$ was assumed to be independent of temperature and 2) the gas phase was assumed to follow the ideal gas law. The temperature dependency can be included in $\Delta_{vap}H^\circ$ approximately by assuming the following form (not a very good approximation either):

$$\Delta_{vap}H = A + BT + CT^2 \quad (6.355)$$

If this is inserted into Eq. (6.351), we get:

$$\frac{dP}{P} = \frac{\Delta_{vap}H}{RT^2} dT = \frac{1}{R} \left(\frac{A}{T^2} + \frac{B}{T} + C \right) dT \quad (6.356)$$

Integration of this equation (without limits) gives the following result:

$$\ln(P) = \frac{1}{R} \left(-\frac{A}{T} + B \ln(T) + CT + D \right) \quad (6.357)$$

where D is a constant of integration.

To see how $\Delta_{vap}H$ can be determined graphically, we integrate Eq. (6.351):

$$\frac{dP}{P} = \frac{\Delta_{vap}H}{RT^2} dT \Rightarrow \int_{P^\circ}^P \frac{dP}{P} = \int_0^T \frac{\Delta_{vap}H}{RT^2} dT$$

and differentiate both sides with respect to T :

$$\frac{d(\ln(P/P^\circ))}{dT} = \frac{\Delta_{vap}H}{RT^2} \Rightarrow \Delta_{vap}H = RT^2 \frac{d(\ln(P/P^\circ))}{dT}$$

By using the chain rule and knowing that $d(1/T)/dT = -1/T^2$, we get:

$$\frac{d(\ln(P/P^\circ))}{dT} = \frac{d(1/T)}{dT} \times \frac{d(\ln(P/P^\circ))}{d(1/T)} = -\frac{1}{T^2} \frac{d(\ln(P/P^\circ))}{d(1/T)}$$

and therefore we have:

$$\Delta_{vap}H = -R \frac{d(\ln(P/P^\circ))}{d(1/T)} \quad (6.358)$$

Notes:

- P above is the vapor pressure (the total external pressure is constant).
- The above form is particularly useful for obtaining a graphical solution because the plot of $-R \times d(\ln(P/P^\circ))/d(1/T)$ gives $\Delta_{vap}H$ (which may or may not be constant).

6.4 Vapor-liquid equilibrium of ideal binary liquid mixtures

Task: To understand vapor-liquid equilibrium when two components are present in a liquid. For example, when we have a mixture of benzene and toluene at a given temperature, what is the vapor composition and the vapor pressure? This consideration would be very important when separating these components by distillation. In this section, we will assume that gases follow the ideal gas law although a more general theory would have to use fugacities instead of partial pressures.

Consider a non-reactive binary component mixture of liquids. When the liquid and vapor phases are in equilibrium, the chemical potentials for each component must equal:

$$\mu_1(l) = \mu_1(g) \text{ and } \mu_2(l) = \mu_2(g) \quad (6.359)$$

For ideal gases the chemical potential for each component in the gas phase is given by Eq. (5.300) with $a_i = P_i/P^\circ$:

$$\mu_i(g) = \mu_i^\circ(g) + RT \ln \left(\frac{P_i}{P^\circ} \right) \text{ where } i = 1, 2 \quad (6.360)$$

For the liquid phase components we have to use the general form (Eq. (4.255)):

$$\mu_i(l) = \mu_i^\circ(l) + RT \ln(a_i) \quad (6.361)$$

By combining the above equations:

$$\mu_i^\circ(g) + RT \ln \left(\frac{P_i}{P^\circ} \right) = \mu_i^\circ(l) + RT \ln(a_i) \quad (6.362)$$

If this equation is written for a pure liquid i , it reads:

$$\mu_i^\circ(g) + RT \ln \left(\frac{P_i^*}{P^\circ} \right) = \mu_i^\circ(l) \quad (6.363)$$

where P_i^* is the equilibrium vapor pressure of pure i . Subtract Eq. (6.363) from (6.362) and we can rearrange the resulting equation as:

$$RT \ln \left(\frac{P_i}{P_i^*} \right) = RT \ln(a_i) \Rightarrow a_i = \frac{P_i}{P_i^*} \quad (6.364)$$

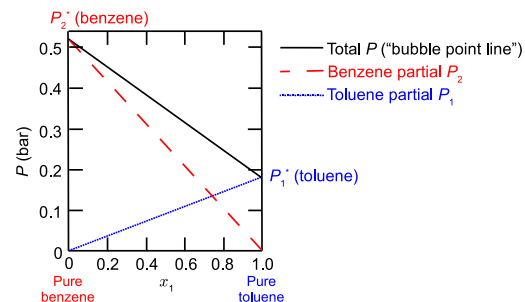
Thus, if the vapor follows the ideal gas law, the activity of a component in a solution is given by the ratio of its partial pressure above the solution to the vapor pressure of the pure liquid.

An experimental finding (Francois-Marie Raoult, 1830 - 1901):

$$P_i \approx x_i P_i^* \text{ (Raoult's law)} \quad (6.365)$$

where P_i^* is the equilibrium pressure of *pure* liquid i and x_i is its molar fraction in *liquid* phase.

This holds well when the components are chemically “similar”. An example of chemically similar compounds is given by a benzene/toluene mixture. The Raoult’s law is demonstrated for this mixture below.



Chemical similarity: A and B are “similar” if the molecular interactions between A – A, A – B and B – B are nearly identical. For the benzene/toluene example, these interactions are long-range van der Waals forces.

Because the gas phase was assumed to be ideal, we can express the partial pressure of a gas component i by multiplying the total gas pressure by the molar fraction in the *gas phase* (y_i):

$$P_i = y_i P \approx x_i P_i^* \quad (6.366)$$

This lets us connect the molar fraction in the liquid phase (x_i) to the gas phase quantities.

From Eq. (6.366) we can solve for x_i (the liquid phase molar fraction):

$$x_i = y_i \frac{P}{P_i^*} = \frac{P_i}{P_i^*} \quad (6.367)$$

Based on Eq. (6.364), the above is equal to activity a_i :

$$a_i = x_i \quad (6.368)$$

Now we have managed to get an expression for activity in the liquid phase by considering the gas phase and the Raoult's law. Inserting this into Eq. (6.21) gives:

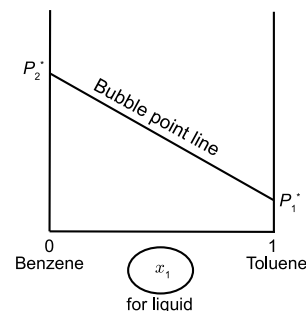
$$\mu_i(l) = \mu_i^\circ(l) + RT \ln \underbrace{(x_i)}_{=a_i} \quad (6.369)$$

Solutions for which Eq. (6.368) holds are called ideal solutions. Recall that y_i is the mole fraction in the gas phase and x_i is the mole fraction in the liquid phase. The total vapor pressure of an ideal binary mixture is given by:

$$P = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = P_2^* + (P_1^* - P_2^*) x_1 \quad (6.370)$$

Why is the total pressure line also called the “bubble point line”?

A liquid boils when its vapor pressure exceeds the external pressure. For example, under normal conditions water boils at 100 °C because at that point its vapor pressure is equal to the atmospheric pressure (1 atm). Boiling is seen as formation of gas bubbles in the liquid. Consider the plot below where the total vapor pressure is shown as a function of x_1 .



If the external pressure would be below the bubble point line, the liquid would start boiling. In the opposite case, the liquid does not boil.

The vapor composition of a binary solution can be calculated using Raoult's law:

$$y_1 = \frac{P_1}{P_1 + P_2} = \frac{x_1 P_1^*}{x_1 P_1^* + x_2 P_2^*} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1} \quad (6.371)$$

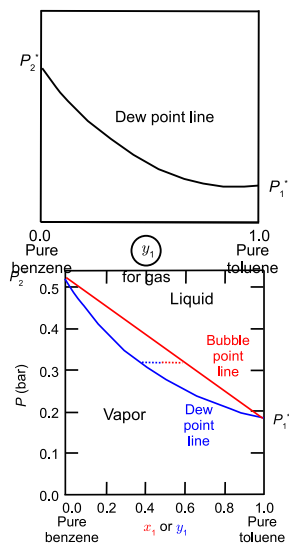
This equation can be solved for x_1 :

$$x_1 = \frac{y_1 P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} \quad (6.372)$$

By eliminating x_1 by using Eq. (6.366), we get:

$$P = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} \quad (6.373)$$

This function is plotted below (i.e., total pressure vs. molar fraction in the gas phase) for benzene/toluene solution:



At external pressures below the dew point line the binary mixture exists as a two-component gas. Above this line liquid starts to form.

P_1^* = Vapor pressure of pure toluene.
 P_2^* = Vapor pressure of pure benzene.

Liquid and vapor compositions for benzene/toluene mixture is shown. Note that the x -axis might be somewhat confusing: it is used for two different variables x_1 and y_1 . This does not mean that they would be equal! Variable x_1 corresponds to the top straight line and y_1 for the lower curve. A tie line (dashed line) connects x_1 and y_1 at a given total pressure P . In the pressure ranges from P_1^* to P_2^* , the system may exist in liquid-gas phase equilibrium with a given x_1 and y_1 .

Example. At 60 °C the vapor pressures of pure benzene and toluene are 0.513 and 0.185 bar, respectively. What are the equations of the bubble point and dew point lines? For a solution with 0.60 mole fraction of toluene, what are the partial pressures of toluene and benzene, and what is the mole fraction of toluene in the vapor? Assume ideal solutions.

Solution. Denote toluene by 1 and benzene by 2. The bubble point line is given by Eq. (6.370):

$$P(x_1) = P_2^* + (P_1^* - P_2^*) x_1 = 0.513 \text{ bar} - (0.328 \text{ bar}) x_1$$

The dew point line is given by Eq. (6.373):

$$P(y_1) = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1} = \frac{0.0949 \text{ bar}^2}{0.185 \text{ bar} - (0.328 \text{ bar}) y_1}$$

With 0.60 mole fraction of toluene, the partial pressures are given by Eq. (6.365):

$$P_1 = x_1 P_1^* = 0.60 \times (0.185 \text{ bar}) = 0.111 \text{ bar}$$

$$P_2 = x_2 P_2^* = 0.40 \times (0.513 \text{ bar}) = 0.205 \text{ bar}$$

From the above bubble point line equation with $x_1 = 0.60$, we get:

$$P = 0.513 \text{ bar} - (0.328 \text{ bar}) \times (0.60) = 0.316 \text{ bar}$$

Eq. (6.371) relates y_1 and x_1 to each other and hence:

$$y_1 = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1} = \frac{0.60 \times (0.185 \text{ bar})}{0.513 \text{ bar} - (0.328 \text{ bar}) \times 0.60} = 0.351$$

Example. Calculate the activities of toluene (component 1) and benzene (component 2) in the liquid by using the values given in the previous example. Assume ideal solutions.

Solution. Use Eq. (6.364):

$$a_1 = \frac{P_1}{P_1^*} = 0.600 \text{ and } a_2 = \frac{P_2}{P_2^*} = 0.400$$

Note that we assumed an ideal solution, the activities are equal to the mole fractions.

Thermodynamic quantities of ideal solutions

In ideal solutions the activities are given by Eq. (6.369): $\mu_i(l) = \mu_i^\circ(l) + RT \ln(x_i)$.

The molar Gibbs energy of a solution at constant T and P is given by Eq. (4.225):

$$\bar{G} = \sum_{i=1}^{N_s} \mu_i \frac{n_i}{n} = \sum_{i=1}^{N_s} \mu_i x_i$$

Inserting the chemical potential expression in above, we get (constant T and P):

$$\bar{G} = \sum_{i=1}^{N_s} x_i \mu_i = \sum_{i=1}^{N_s} x_i \mu_i^\circ + RT \sum_{i=1}^{N_s} x_i \ln(x_i) \quad (6.374)$$

Note that this expression gives the molar Gibbs energy as a function of pressure and temperature. Thus this expression contains all of the thermodynamic information about an ideal solution.

The molar entropy of an ideal solution can be obtained using Eqs. (4.221) and (4.227):

$$\bar{S} = - \left(\frac{\partial \bar{G}}{\partial T} \right)_P = - \sum_{i=1}^{N_s} x_i \left(\frac{\partial \mu_i^\circ}{\partial T} \right)_P - R \sum_{i=1}^{N_s} x_i \ln(x_i) = \sum_{i=1}^{N_s} x_i S_i^\circ - R \sum_{i=1}^{N_s} x_i \ln(x_i) \quad (6.375)$$

The molar enthalpy of an ideal solution can be calculated by using the Gibbs-Helmholtz equation (using Eqs. (4.241), (4.227) with $\bar{G}_i^\circ = \mu_i^\circ$, and $\bar{G}_i^\circ = \bar{H}_i^\circ - T\bar{S}_i^\circ$):

$$\begin{aligned} \bar{H} &= -T^2 \left[\frac{\partial (\bar{G}/T)}{\partial T} \right]_{P, \{n_i\}} = -T^2 \sum_{i=1}^{N_s} \left[x_i \frac{\partial (\mu_i^\circ/T)}{\partial T} \right] = -T^2 \sum_{i=1}^{N_s} \left[x_i \left(\frac{1}{T} \frac{\partial \mu_i^\circ}{\partial T} - \frac{\mu_i^\circ}{T^2} \right) \right] \\ &= \sum_{i=1}^{N_s} x_i \left(-T \frac{\partial \mu_i^\circ}{\partial T} + \mu_i^\circ \right) = \sum_{i=1}^{N_s} x_i (T\bar{S}_i^\circ + \bar{G}_i^\circ) = \sum_{i=1}^{N_s} x_i \bar{H}_i^\circ \end{aligned} \quad (6.376)$$

The molar volume is obtained from Eq. (4.222):

$$\bar{V} = \left(\frac{\partial \bar{G}}{\partial P} \right)_{T, \{n_i\}} = \left(\partial \left[\sum x_i \overbrace{RT \ln(x_i)}^{=\mu_i - \mu_i^\circ(6.369)} \right] / \partial P \right) = \sum x_i (\partial \mu_i / \partial P) = \sum_{i=1}^{N_s} x_i \bar{V}_i \quad (6.377)$$

Remember above that μ_i° does not depend on pressure - only on temperature.

The first terms (with superscripts $^\circ$) in Eqs. (6.374) and (6.375) give the thermodynamic properties of isolated species (i.e. no mixing) and the possible second term the effect of mixing:

$$\Delta_{mix} G = RT \sum_{i=1}^{N_s} x_i \ln(x_i) \quad (6.378)$$

$$\Delta_{mix} S = -R \sum_{i=1}^{N_s} x_i \ln(x_i) \quad (6.379)$$

$$\Delta_{mix} H = 0 \quad (6.380)$$

$$\Delta_{mix} V = 0 \quad (6.381)$$

These results are essentially the same as we obtained earlier for ideal gas mixtures. *Note that there is no volume change or heat evolution when ideal solutions are formed under constant temperature and pressure.*

The effect of temperature on ideal binary liquid mixtures at constant pressure

Consider toluene (1) - benzene (2) mixture at atmospheric pressure (units in bar):

	80.1 °C	88 °C	90 °C	94 °C	98 °C	100 °C	104 °C	110.6 °C
P_1^*	–	0.508	0.543	0.616	0.698	0.742	0.836	<u>1.013</u>
P_2^*	<u>1.013</u>	1.285	1.361	1.526	1.705	1.800	2.004	–

The boiling points for pure liquids were underlined above. Vapor pressures for pure liquids can be determined experimentally.

Example. Calculate the liquid mole fraction (x_1) of toluene in benzene-toluene solution that boils at 100 °C. Calculate also the toluene mole fraction (y_1) in the vapor above the liquid.

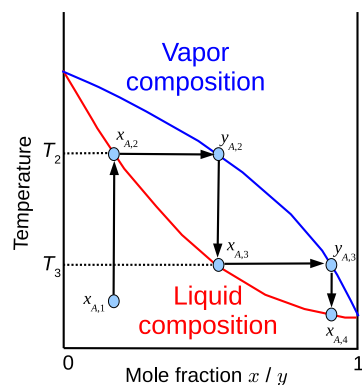
Solution. We use Eq. (6.370) and solve for x_1 , recall that a liquid boils when its vapor pressure reaches the external pressure (one atmosphere here) and use the above table:

$$x_1 = \frac{P - P_2^*}{P_1^* - P_2^*} = \frac{(1.013 \text{ bar}) - (1.800 \text{ bar})}{(0.742 \text{ bar}) - (1.800 \text{ bar})} = 0.744$$

By knowing x_1 , we can further use Eq. (6.366) to get y_1 :

$$y_1 = \frac{x_1 P_1^*}{P} = \frac{0.744 \times (0.742 \text{ bar})}{1.013 \text{ bar}} = 0.545$$

Example. The method of fractional distillation can be understood in the previously developed theory. Consider a binary ideal mixture with components A and B. In this example component A (i.e., the volatile component) has a lower boiling point than B.

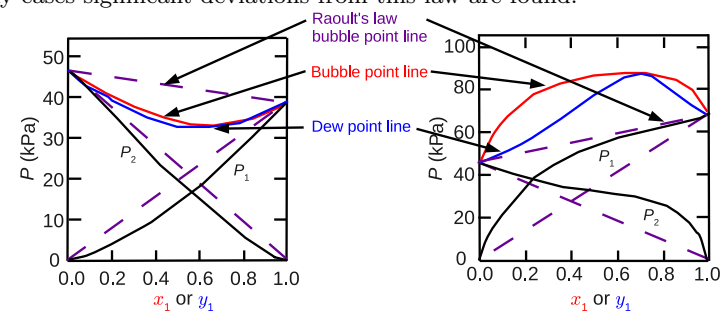


1. Consider a solution with mole fraction $x_{A,1}$ of A.
2. Heat the solution to its boiling point T_2 . The liquid mole fraction is now $x_{A,2}$.
3. Extract vapor, which has mole fraction $y_{A,2}$. Note that there is more of the volatile component in the gas phase than in the liquid.

Repeat the above cycle for the liquid, which was condensed from the gas phase above. The next step is shown as $x_{A,3}$ and $y_{A,3}$. By repeating the cycle, a better separation of the components can be reached.

6.5 Vapor pressure of nonideal mixtures

In the previous section we assumed that Raoult's law holds (Eq. (6.365)). However, in many cases significant deviations from this law are found:

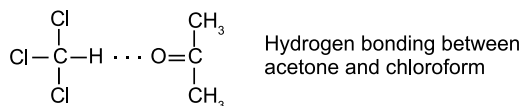


Liquid mixture with a negative azeotrope. (1) chloroform and (2) acetone at 35.17 °C. Note that the bubble point and the dew point lines overlap. The dashed line shows the results from Raoult's law.

Liquid mixture with a positive azeotrope. (1) carbon disulfide and (2) acetone at 35.17 °C.

The points where the bubble point and dew point lines cross, are called *azeotropic points*. In this case distillation can not separate the components!

What is the origin of the deviation from the Raoult's law?



This extra binding interaction lowers the vapor pressure from that predicted by the Raoult's law. The maximum effect is seen when there are equal amounts of the components (i.e. the middle of the bubble point line on previous slide).

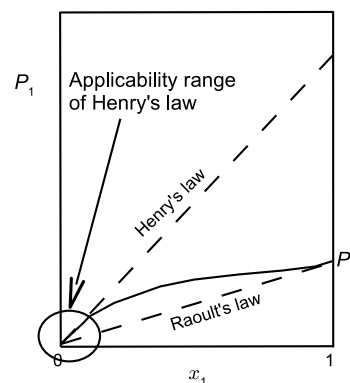
A positive trend (i.e. the bubble point line is above the Raoult's law prediction) is observed when A – A and B – B interactions are stronger than A – B. Here A and B are the components forming the binary mixture. If these deviations are large enough, the system separates into two phases A and B.

Henry's law attempts to fix the deficiency of the Raoult's at small mole fractions, which are close to zero or one (i.e. nearly one component solutions). It consists of the following linear approximation:

$$P_i = K_i x_i \quad (6.382)$$

where K_i is Henry's law constant for component i . Its value can be obtained from plotting the ratio P_i/x_i when x_i approaches zero.

Behavior of the partial pressures as a function of x_i (the liquid phase mole fraction) is shown below for Henry's law, Raoult's law and the experimental data (continuous line):



Henry's law constants given in Pascals (25 °C).

Gas	Water	Benzene
H ₂	7.12×10^9	0.367×10^9
N ₂	8.68×10^9	0.239×10^9
O ₂	4.40×10^9	–
CO	5.79×10^9	0.163×10^9
CO ₂	0.167×10^9	0.0114×10^9
CH ₄	4.19×10^9	0.0569×10^9
C ₂ H ₂	0.135×10^9	–
C ₂ H ₄	1.16×10^9	–
C ₂ H ₆	3.07×10^9	–

The most common application of Henry's law is to calculate solubilities of gases in liquids. In this case the amounts of dissolved gas is very small, which means that its molar fraction in the liquid is small.

Example. Use the Henry's law constant, calculate the solubility of carbon dioxide in water at 25 °C in moles per liter at a partial pressure of CO₂ over the solution of 1 bar. Assume that 1 L of solution contains approximately 1000 g of water.

Solution. We apply Henry's law (Eq. (6.382)). Denote water by component 1 and CO₂ by component 2. The partial pressure of CO₂ in the gas phase was given as: $P_2 = 10^5$ Pa. Now Eq. (6.382) gives:

$$x_2 = \frac{P_2}{K_2} = \frac{10^5 \text{ Pa}}{0.167 \times 10^9 \text{ Pa}} = 6.0 \times 10^{-4}$$

By the definition of mole fraction, we have:

$$x_2 = \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{H}_2\text{O}]} \approx \frac{[\text{CO}_2]}{[\text{H}_2\text{O}]}$$

$$\Rightarrow [\text{CO}_2] = x_2 [\text{H}_2\text{O}] = (6.0 \times 10^{-4}) \times (55.5 \text{ mol L}^{-1}) = 3.3 \times 10^{-2} \text{ mol L}^{-1}$$

Notes:

- ▶ The solubility of a gas in liquids usually decreases with increasing temperature because heat is generally evolved in the solvation process.
- ▶ There are exceptions to this - especially with solvents like liquid ammonia, molten silver and some organic liquids.
- ▶ Solubility of an unreactive gas in a liquid is due to intermolecular attractive forces (van der Waals forces) between gas molecules and solvent molecules.
- ▶ Addition of electrolytes (i.e. ionic species) usually decreases solubility of gases in liquids ("salting out").

If the vapor pressure of a solute follows Henry's law, then we can insert Eq. (6.382) into Eq. (6.360):

$$\mu_i(g) = \mu_i^\circ(g) + RT \ln \left(\frac{K_i x_i}{P^\circ} \right) \quad (6.383)$$

At equilibrium $\mu_i(g) = \mu_i(l)$ (see Eq. (6.359)) and expanding the logarithm gives:

$$\mu_i(l) = \underbrace{\mu_i^\circ(g) + RT \ln \left(\frac{K_i}{P^\circ} \right)}_{=\mu_i^*(l)} + RT \ln(x_i) = \mu_i^*(l) + RT \ln(x_i) \quad (6.384)$$

where we introduced the standard chemical potential for species i in the liquid:

$$\mu_i^*(l) = \mu_i^\circ(g) + RT \ln \left(\frac{K_i}{P^\circ} \right) \quad (6.385)$$

Note that the above standard state is hypothetical because it corresponds to $x_i = 1$ for the solute but it is still taken to be dilute solution. Even as such, this state is useful as a reference. For this reason, dilute solutions are not the same as ideal solutions.

6.6 Activity coefficients

It is convenient to relate activity to liquid mole fraction:

$$a_i = \gamma_i x_i \quad (6.386)$$

where γ_i is the activity coefficient for species i . With this notation, Eq. (6.361) reads:

$$\mu_i(l) = \mu_i^\circ(l) + RT \ln(\gamma_i x_i) \quad (6.387)$$

Note that when $x_i \rightarrow 1$ then $\gamma_i \rightarrow 1$ because it approaches a pure liquid. For positive deviations from Raoult's law, $\gamma_i > 1$ and $\gamma_i < 1$ for negative deviations. Combining Eqs. (6.364) and (6.386) we have:

$$a_i = \gamma_i x_i = \frac{P_i}{P_i^*} \quad (6.388)$$

From this expression, we can calculate the activity coefficient by using experimental data:

$$\gamma_i = \frac{P_i}{x_i P_i^*} \quad (6.389)$$

For ideal gases we have $P_i = y_i P$ and the above equation can be written in this case:

$$\gamma_i = \frac{y_i P}{x_i P_i^*} \quad (6.390)$$

Above the activity coefficient is written with *reference to Raoult's law*.

Activity coefficients can also be expressed with reference to Henry's law. To see this, we first express the activity as a product of the activity coefficient (denoted by prime to differentiate it from the activity coefficient with Raoult's law reference):

$$\mu_i(l) = \mu_i^*(l) + RT \ln(\gamma'_i x_i) \quad (6.391)$$

By combining Eqs. (6.359) and (6.360) we get:

$$\mu_i(l) = \mu_i^\circ(g) + RT \ln\left(\frac{P_i}{P^\circ}\right) \quad (6.392)$$

Next recall Eq. (6.385): $\mu_i^*(l) = \mu_i^\circ(g) + RT \ln\left(\frac{K_i}{P^\circ}\right)$

By substituting the above two expressions into Eq. (6.391), the following modified form for Henry's law can be obtained:

$$P_i = \gamma'_i K_i x_i \quad (6.393)$$

This allows us to calculate the activity coefficient γ'_i :

$$\gamma'_i = \frac{P_i}{x_i K_i} \rightarrow 1 \text{ when } x_i \rightarrow 0 \quad (6.394)$$

Since $P_i = y_i P$, this can also be written as:

$$\gamma'_i = \frac{y_i P}{x_i K_i} \quad (6.395)$$

What is the principal difference between γ_i and γ'_i ?

γ_i (*Raoult's law reference*) has a reference state, which consists of an ideal solution. The chemical potential corresponding to this standard state is denoted by μ_i° .

γ'_i (*Henry's law reference*) has a reference state, where each molecule of the solute has the same interactions that it experiences in very dilute solutions. The chemical potential corresponding to this standard state is denoted by μ_i^* .

Thus the only difference is that they have different reference states.

Example. Calculate the activity coefficients γ_i for ether (component 1) and acetone (component 2) in 1:1 ether-acetone solutions at 30 °C. The experimental data are given in the table below.

Table. Activity coefficients for acetone-ether solutions at 30 °C. 1 = ether, 2 = acetone. Pressure is given in kPa.

Raoult's law reference							Henry's law reference	
x_2	P_1	$x_1 P_1^*$	γ_1	P_2	$x_2 P_2^*$	γ_2	$K_2 x_2$	γ'_2
0	86.1	86.1	1.0	0	0	—	0	1.00
0.2	71.3	68.9	1.04	12.0	7.5	1.60	15.7	0.77
0.4	58.7	51.7	1.14	19.7	15.1	1.31	31.4	0.63
0.5	52.1	43.1	1.21	22.4	18.9	1.19	39.2	0.57
0.6	44.3	34.4	1.28	25.3	22.7	1.12	47.0	0.54
0.8	26.9	17.3	1.56	31.3	30.1	1.04	62.7	0.50
1.0	0	0	—	37.7	37.7	1.00	78.4	0.48

Solution. At 0.5 mole fraction, the activity coefficients of the two components are given by:

$$\gamma_1 = \frac{P_1}{x_1 P_1^*} = \frac{52.1 \text{ kPa}}{43.1 \text{ kPa}} = 1.21$$

$$\gamma_2 = \frac{P_2}{x_2 P_2^*} = \frac{22.4 \text{ kPa}}{18.9 \text{ kPa}} = 1.19$$

Note that the Henry's law activity coefficient γ'_i can be calculated from the data given in the previous table by extrapolating to $x_2 = 0$ when calculating $K_2 = P_2/x_2$ (see Eq. (6.382)).

What is the relation between γ_i and γ'_i ?

According to Eq. (6.364) the activity of a real solution is given by $a_i = P_i/P_i^*$. Substitution of Eq. (6.394) there gives:

$$a_i = \frac{\gamma'_i K_i x_i}{P_i^*} \quad (6.396)$$

With $a_i = \gamma_i x_i$ this gives:

$$\gamma_i = \frac{\gamma'_i K_i}{P_i^*} \text{ or } \gamma'_i = \frac{\gamma_i P_i^*}{K_i} \quad (6.397)$$

Notes:

- ▶ For dilute solutions, the solvent is usually treated on the basis of deviations from Raoult's law and the solute is usually treated on the basis of deviations from Henry's law.
- ▶ Three different concentration scales can be used with Henry's law:
 $P_i = K_i m_i$ where m_i is the molal concentration of i (mol / kg of solvent),
 $P_i = K_i c_i$ where c_i is the molar concentration of i (mol / L of solution), or
 $P_i = K_i x_i$ where x_i is the (liquid) molar fraction.
- ▶ Since we mostly calculate differences in a given thermodynamic variable, the reference (= standard) state usually cancels out. However, both initial and final states must be expressed with respect to the same reference state.

6.7 Colligative properties

Colligative properties: depression of freezing point, elevation of boiling point, osmotic pressure, and the lowering of the vapor pressure by a non-volatile solute.

The depression of freezing point

Consider an ideal mixture of solvent A and solute B (i.e. A is in excess of B). The phase equilibrium between solid A and liquid A is given by Eqs. (6.359) and (6.361) (also note that for solids $\mu^\circ = \mu$ and for ideal solutions $a_i = x_i$):

$$\mu_A^\circ(s, T) = \mu_A(s, T) = \mu_A(l, T) = \mu_A^\circ + RT \ln(a_A) = \mu_A^\circ + RT \ln(x_A) \quad (6.398)$$

Solving for $\ln(x_A)$ we get:

$$\ln(x_A) = \frac{\mu_A^\circ(s, T) - \mu_A^\circ(l, T)}{RT} = -\frac{\Delta_{fus} G_A^\circ(l, T)}{RT} \quad (6.399)$$

where $\Delta_{fus} G_A^\circ$ is the Gibbs energy of fusion at temperature T .

Next we assume that $\Delta_{fus}H^\circ$ and $\Delta_{fus}S^\circ$ are independent of temperature near the freezing point of A (Eq. (3.176) and constant P):

$$\Delta_{fus}G_A^\circ = \Delta_{fus}H_A^\circ - T\Delta_{fus}S_A^\circ = \Delta_{fus}H_A^\circ - T\left(\frac{\Delta_{fus}H_A^\circ}{T_{fus,A}}\right) = \Delta_{fus}H_A^\circ \left(1 - \frac{T}{T_{fus,A}}\right) \quad (6.400)$$

When this is substituted into Eq. (6.399), we have:

$$\ln(x_A) = -\left(\frac{\Delta_{fus}H_A^\circ}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{fus,A}}\right) = -\left(\frac{\Delta_{fus}H_A^\circ}{R}\right)\left(\frac{T_{fus,A} - T}{T_{fus,A}T}\right) \quad (6.401)$$

Next we relate x_A to x_B by $x_A = 1 - x_B$ (also $T \approx T_{fus,A}$):

$$\ln(x_A) = \ln(1 - x_B) \approx -\frac{\Delta_{fus}H_A^\circ}{RT_{fus,A}^2} \times \underbrace{(T_{fus,A} - T)}_{=\Delta T_f} = -\frac{\Delta_{fus}H_A^\circ \Delta T_f}{RT_{fus,A}^2} \quad (6.402)$$

This expression can be approximated by using the Taylor expansion of $\ln(1 - x)$:

$$\begin{aligned} \ln(1 - x) &= -x - \frac{1}{2}x^2 - \frac{1}{3}x^3 - \dots \text{ when } -1 < x < 1 \\ &\approx -x \text{ when higher order terms are ignored. Here } x \approx 0 \end{aligned} \quad (6.403)$$

With this approximation, Eq. (6.402) can be written as:

$$\Delta T_f = \left(\frac{RT_{fus,A}^2}{\Delta_{fus}H_A^\circ}\right)x_B \quad (6.404)$$

Where ΔT_f indicates the change (i.e., depression) in freezing point. In this context the concentration is often given in terms of molal concentrations m (i.e., moles of solute per kg of solvent; not mass here!) and M in kg mol^{-1} . The relationship between molal concentration and mole fraction for B is:

$$x_B = \frac{n_B}{n_A + n_B} = \frac{n_B/(M_A n_A)}{(n_A + n_B)/(M_A n_A)} = \frac{m_B}{1/M_A + m_B} \approx m_B M_A \quad (6.405)$$

where M_A is the molar mass of A. The last approximation applies to dilute solution. Substitution of Eq. (6.405) into (6.404) gives (K_f is called the *freezing point constant*):

$$\Delta T_f = \frac{RT_{fus,A}^2 M_A m_B}{\Delta_{fus}H_A^\circ} = K_f m_B \text{ with } K_f = \frac{RT_{fus,A}^2 M_A}{\Delta_{fus}H_A^\circ} \quad (6.406)$$

The elevation of boiling point

By using analogous approach to obtain the depression of freezing point, we can obtain the following expressions for the elevation of boiling point:

$$\Delta T_b = \frac{RT_{vap,A}^2}{\Delta_{vap}H_A^\circ} x_B = K_b m_B \text{ where } K_b = \frac{RT_{vap,A}^2 M_A}{\Delta_{vap}H_A^\circ} \quad (6.407)$$

Example. Denote the solvent by A and the solute by B. Derive an expression for the molar mass of B in terms of $(K_b, \Delta T_b)$ or $(K_f, \Delta T_f)$. Assume that the mass of B dissolved in A and the total weight of the solution are given and that the solution is dilute in B.

Solution. Since the solution is dilute in B, we have approximately $\text{mass}(A) \approx \text{mass}(A + B)$, where $\text{mass}(A)$ is the mass of solvent A (kg) and $\text{mass}(A + B)$ is the mass of the solution containing both A and B. Since $m_B = \text{“moles of solute molecules dissolved”} / \text{“the total mass of the solvent”}$, we can write:

$$m_B = \frac{n_B}{\text{mass}(A)} \approx \frac{n_B}{\text{mass}(A + B)}$$

On the other hand we have:

$$\Delta T_b = K_b m_B \text{ or } \Delta T_f = K_f m_B$$

By combining the above equations, we get:

$$n_B = \frac{\Delta T_f}{K_f} \times \text{mass}(A + B) \text{ or } n_B = \frac{\Delta T_b}{K_b} \times \text{mass}(A + B)$$

$$\Rightarrow \text{M.W. of B} = \frac{\text{mass}(B)}{n_B} = \frac{K_f}{\Delta T_f} \times \frac{\text{mass}(B)}{\text{mass}(A + B)} \text{ in units of kg mol}^{-1}$$

This allows for determination of the molecular mass of B experimentally provided that the constants K_f (aka. cryoscopic constant) or K_b (aka. ebullioscopic constant) are known. Their values for few selected solvents are shown below.

Table. Cryoscopic and ebullioscopic constants for selected solvents.

Solvent	K_f (K kg mol ⁻¹)	K_b (K kg mol ⁻¹)
Benzene	5.12	2.53
Camphor	40	—
Phenol	7.27	3.04
Water	1.86	0.51

6.8 Two-component systems consisting of solid and liquid phases

When a solid solute (A) is left in contact with a solvent (B), it dissolves until the solution is saturated. In this case saturation is a state of equilibrium with the undissolved solute in equilibrium with the dissolved solute. Therefore, in a saturated solution the chemical potential of the pure solid solute ($\mu_A(s, T)$) and the chemical potential of A in solution ($\mu_A(l, T)$) are equal. The derivation below is essentially the same as given earlier in Eqs. (6.398) through (6.401).

By using Eq. (6.369), we can write for A:

$$\mu_A(l, T) = \mu_A^\circ(l, T) + RT \ln(x_A)$$

Because there is equilibrium between the solid and dissolved forms of A, we have:

$$\mu_A(l, T) = \mu_A(s, T)$$

Furthermore, pure solids have chemical potential equal to that of standard state:

$$\mu_A(s, T) = \mu_A^\circ(s, T) \Rightarrow \mu_A(l, T) = \mu_A^\circ(s, T)$$

Inserting this into the first equation, we get:

$$\mu_A^\circ(s, T) = \mu_A^\circ(l, T) + RT \ln(x_A)$$

If we solve for $\ln(x_A)$, the expression becomes (with $G = H - TS$):

$$\ln(x_A) = \frac{\mu_A^\circ(s, T) - \mu_A^\circ(l, T)}{RT} = -\frac{\Delta_{fus}G_A^\circ}{RT} = -\frac{\Delta_{fus}H_A^\circ}{RT} + \frac{\Delta_{fus}S_A^\circ}{R}$$

Note that above \circ refers to the standard state of A (1 bar pressure and pure solute).

At constant P and T , we can use Eq. (3.176) and replace $\Delta_{fus}S$:

$$\begin{aligned} \Delta_{fus}S_{A^\circ} &= \frac{\Delta_{fus}H_A^\circ}{T_{fus,A}} \Rightarrow \ln(x_A) = -\frac{\Delta_{fus}H_A^\circ}{RT} + \frac{\Delta_{fus}H_A^\circ}{RT_{fus,A}} \\ &\Rightarrow \ln(x_A) = -\frac{\Delta_{fus}H_A^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_{fus,A}} \right) \end{aligned}$$

Solving for x_A gives:

$$x_A = \exp \left(-\frac{\Delta_{fus}H_A^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_{A,fus}} \right) \right) \quad (6.408)$$

This expression gives the solubility of A in B as a function of temperature when $\Delta_{fus}H_A^\circ$ is known.

Chapter 7: Electrochemical equilibrium

“An understanding of the conversion of chemical energy to electrical energy is important for work with batteries, fuel cells, electroplating, corrosion, electrorefining and electroanalytical techniques”.

7.1 Coulomb’s law, electric field, and electric potential ²⁹⁸

The force \vec{f} between two point charges (denoted by 1 and 2) is given by the Coulomb’s law:

$$\vec{f} = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{Q_1Q_2}{r^2} \vec{r} \quad (7.409)$$

where:

- r = distance between the charges
- Q_1 = charge of particle 1
- Q_2 = charge of particle 2
- ϵ_0 = permittivity of vacuum (constant; $8.854\,187\,817 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$)
- ϵ_r = relative permittivity (dielectric constant) of the material (solid, gas, etc.)
- \vec{r} = unit vector connecting charges 1 and 2.

When only the magnitude of the force is considered, the above equation becomes:

$$f = \frac{Q_1Q_2}{4\pi\epsilon_0\epsilon_r r^2} \quad (7.410)$$

The electric field strength at point 1 is given by the ratio between force and the charge Q_1 :

$$\vec{E} = \frac{\vec{f}}{Q_1} \quad (7.411)$$

For each well behaved vector field (i.e. conservative) there is a potential ϕ such that:

$$\vec{E} = -\vec{\nabla}\phi \quad (7.412)$$

Note that here $\phi = \phi(x, y, z)$ and E is a vector-field with components $(E_x(x, y, z), E_y(x, y, z), E_z(x, y, z))$. Gradient ($\vec{\nabla}$) is an example of a vector operator:

$$\vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

Example. Calculate the gradient vector for function $f(x, y, z) = x^2 + y^2 + z^2$ and find the point where the length of the gradient vector becomes zero.

Solution. Calculate the partial derivatives of f with respect to x, y and z :

$$\frac{\partial f}{\partial x} = 2x, \frac{\partial f}{\partial y} = 2y, \frac{\partial f}{\partial z} = 2z$$

$$\Rightarrow \vec{\nabla}f = (2x, 2y, 2z). \text{ When } x = 0, y = 0, z = 0, \text{ then } \left| \vec{\nabla}f \right| = 0.$$

Note that function f has its (global) minimum at this point.

Definition of 1 Volt (V): In presence of the electric field (from Q_2), the difference between the electric potential at two points is equal to the work per unit charge required to move a charged test particle from one point to the other. Thus $1 \text{ V} = 1 \text{ J C}^{-1}$. The choice of zero potential is arbitrary but is usually chosen to correspond to infinite separation of charges.

The electric potential ϕ at point r is the work required to bring a unit positive charge from infinity to r . Combining Eqs. (7.409) and (7.412) and integrating from infinity to r gives:

$$\phi(r) = -\frac{Q_2}{4\pi\epsilon_0\epsilon_r} \int_{\infty}^r \frac{dr'}{r'^2} = \frac{Q_2}{4\pi\epsilon_0\epsilon_r r} \quad (7.413)$$

In electrolyte solutions we have electroneutrality condition:

$$\sum_{i=1}^{N_P} n_i z_i = 0 \quad (7.414)$$

where N_P is the number of phases, n_i is the amount of ions in phase i and $z_i \times e$ is the charge of ions (e = charge of one proton; $1.6022 \times 10^{-19} \text{ C}$). The charge z_i is positive for cations and negative for anions. For a phase to have a non-zero electric potential, there must be a small deviation from Eq. (7.414) but these deviations are small and we can still say that it holds (to good approximation).

7.2 Equilibria involving potential differences

Recall Eq. (2.95): $dw = \phi dQ$ (ϕ = potential, dQ = differential charge)

Recall Eq. (4.220): $dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu'_i dn_i + \sum_{i=1}^{N_s} \phi_i dQ_i$

The change in total charge Q is given by:

$$dQ_i = z_i F dn_i \quad (7.415)$$

where z_i is the charge of species i , F is the Faraday constant ($F = N_A \times e$; 96485.309 C mol⁻¹), dn_i is the change in the number of ions (mol) and ϕ_i is the electric potential of the phase containing species i . The prime on the chemical potential signifies the fact that it is the pure chemical potential (i.e., not including the electrical work). Note that z_i is dimensionless where dQ has units of C.

By combining Eqs. (4.220) and (7.415) we get:

$$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu'_i dn_i + F \sum_{i=1}^{N_s} z_i \phi_i dn_i = -SdT + VdP + \sum_{i=1}^{N_s} \underbrace{(\mu'_i + Fz_i \phi_i)}_{\equiv \mu_i} dn_i \quad (7.416)$$

This means that the chemical potential μ_i can be taken to contain the electrical work as well:

$$\mu_i = \mu'_i + z_i F \phi_i \quad (7.417)$$

The equilibrium condition Eq. (6.347) still applies: $\mu_i(\alpha) = \mu_i(\beta)$ for species i and phases α and β .

7.3 Equation for an electrochemical cell

Galvanic cells: Electrochemical cells where chemical reactions occur spontaneously.

Examples of galvanic cells: Zn/MnO₂ and Zn/Ag₂O₃ cells used in watches etc.; H₂/O₂ fuel cell used in spacecrafts.

Electrolytic cells: Electrochemical cells where a chemical reaction is driven by an external potential difference.

Examples of electrolytic cells: Pb/PbO₂/H₂SO₄ cell used in automobile batteries etc.; commercial production of chlorine and aluminum; electrorefining of copper.

Cathode is the electrode where the reduction occurs:

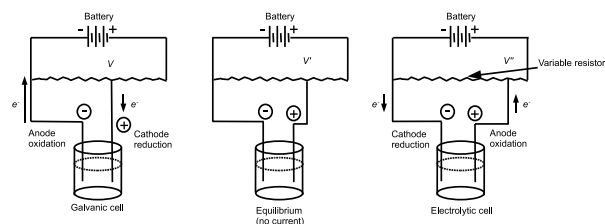


Anode is the electrode where the oxidation occurs:



In galvanic cell: + = Cathode (reduction) and - = Anode (oxidation).

In electrolytic cell: + = Anode (oxidation) and - = Cathode (reduction).



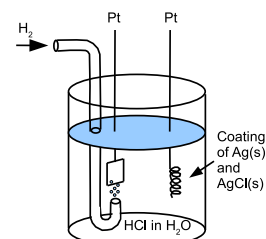
Determination of the potential difference between two electrodes by a potentiometer.

- Galvanic cell*: the external potential V (battery + variable resistor) is less than the cell potential E . The process is spontaneous (i.e. proceeds without the help from the battery).
- Equilibrium*: the external potential V' (battery + variable resistor) is equal to the cell potential E . Note that now no current flows in the system.
- Electrolytic cell*: the external potential V'' (battery + variable resistor) is greater than the cell potential E . The process is nonspontaneous (i.e. driven by the battery).

Notes:

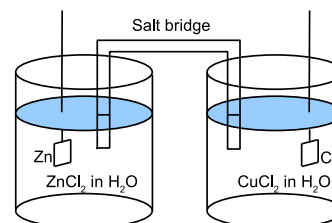
- ▶ Voltage is the energy difference per charge (electron) ($V = J / C$).
- ▶ Current is the number of charged particles (electrons) flowing per second ($A = C / s$). Since $V = J / C$ then $e \times V$ (eV for short) is a unit energy (electron volts).

Cells without junctions:



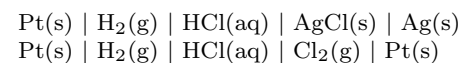
Galvanic cell without junction.

Cells with liquid junctions:

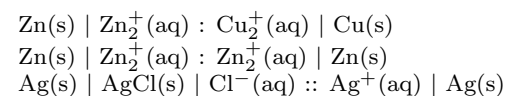


Galvanic cell with junction (Daniel cell).

Examples:



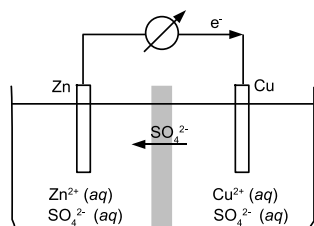
Examples:



: = liquid junction

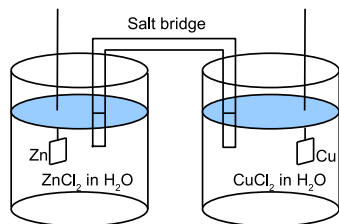
:: = salt bridge

An example of liquid junction:



Daniel cell with a diaphragm.

An example of salt bridge:



Galvanic cell with junction (Daniel cell).

The liquid compartments have been separated by a diaphragm, which lets only the ions through but does not let the two solutions to mix.

The liquid compartments have been separated by a salt bridge, which lets only the ions through but does not let the two solutions to mix. The bridge can be a U-tube filled with NaCl electrolyte, for example.

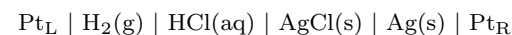
The electromotive force (EMF) of a cell is denoted by E (V) and it is defined by:

$$P = \frac{d(-w_{el})}{dt} = EI \quad (7.420)$$

where w_{el} is the electrical work done by the system (negative), P is the rate at which chemical energy is converted to electrical energy (W) and I is the current (A).

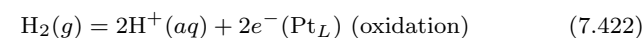
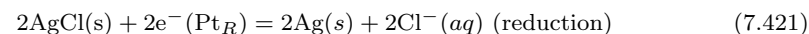
Task: What is the relation between the electromotive force in a cell and the chemical potentials (or ion activities) in the cell?

To do this, let's consider an example (L = left, R = right):

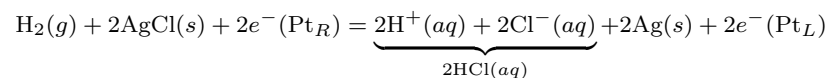


Note that the convention is that reduction takes place on the right electrode and oxidation occurs in the left electrode.

The electrode reactions are:



By combining the above, we get:



Consider a cell without any external connections to the electrode (see, for example, the previous galvanic cell without liquid junction example; i.e. open circuit). For such a system in equilibrium, we must have (similar to Eq. (6.347)):

$$2\mu(\text{HCl}, aq) + 2\mu(\text{Ag}, s) + 2\mu(e^-, \text{Pt}_L) = \mu(\text{H}_2, g) + 2\mu(\text{AgCl}, s) + 2\mu(e^-, \text{Pt}_R) \quad (7.423)$$

Each chemical potential here is given by Eq. (7.417): $\mu_i = \mu'_i + z_i F \phi_i$

For all neutral species (HCl, Ag, H₂, AgCl) $\mu_i = \mu'_i$ because $z_i = 0$.

Right electrode: $\mu(e^-, \text{Pt}_R) = \mu'(e^-, \text{Pt}_R) - F \phi_R$

Left electrode: $\mu(e^-, \text{Pt}_L) = \mu'(e^-, \text{Pt}_L) - F \phi_L$

Now $\mu'_i(e^-, \text{Pt}_R) = \mu'_i(e^-, \text{Pt}_L)$. To see this, consider that the left and right electrodes are in contact (i.e. $\phi_L = \phi_R$) and we have equilibrium $\mu_i(e^-, \text{Pt}_R) = \mu_i(e^-, \text{Pt}_L)$. By considering the above two equations with these conditions, we get $\mu'_i(e^-, \text{Pt}_R) = \mu'_i(e^-, \text{Pt}_L)$.

By plugging these results into Eq. (7.423), we get:

$$\begin{aligned} 2\mu(\text{HCl}, aq) + 2\mu(\text{Ag}, s) - 2F\phi_L &= \mu(\text{H}_2, g) + 2\mu(\text{AgCl}, s) - 2F\phi_R \quad (7.424) \\ \text{or } 2\mu(\text{HCl}, aq) + 2\mu(\text{Ag}, s) - \mu(\text{H}_2, g) - 2\mu(\text{AgCl}, s) &= 2F(\phi_L - \phi_R) \end{aligned}$$

For a “normal” chemical reaction ($\text{H}_2(g) + 2\text{AgCl}(s) = 2\text{HCl}(aq) + 2\text{Ag}(s)$), we would have:

$$\Delta_r G = 2\mu(\text{HCl}, aq) + 2\mu(\text{Ag}, s) - \mu(\text{H}_2, g) - 2\mu(\text{AgCl}, s)$$

By combining this with Eq. (7.424), we get:

$$\Delta_r G = -2F(\phi_R - \phi_L) = -2FE \text{ with } E = \phi_R - \phi_L \quad (7.425)$$

Note that E is considered here in the limit of zero current. Since $\Delta_r G$ depends on pressure and temperature, the cell potential difference depends on P and T as well. Also the concentration of HCl affects the the potential difference.

Although the above derivation applies only to a special case, it is clear that the general equation corresponding to Eq. (7.425) is:

$$\Delta_r G = -|v_e| FE \quad (7.426)$$

where v_e is the number of electrons transferred (“charge number”). Note that when the right-hand side electrode has a more positive potential than the left-hand electrode, the electromotive force E for the cell is positive. If E is positive, $\Delta_r G$ is negative (Eq. (7.426)) and the cell reaction is spontaneous at constant P and T . According to Eq. (7.425) this occurs when $\phi_R > \phi_L$.

By combining Eqs. (5.297) and (4.255) with (7.426), we get:

$$\begin{aligned} -|v_e| FE = \Delta_r G &= \underbrace{\sum_{i=1}^{N_s} v_i \mu_i^\circ}_{\equiv -|v_e| FE^\circ} + RT \sum_{i=1}^{N_s} v_i \ln(a_i) = -|v_e| FE^\circ + RT \ln \left(\prod_{i=1}^{N_s} a_i^{v_i} \right) \quad (7.427) \end{aligned}$$

309

where E° is the standard electromotive force of the cell (i.e. the EMF when the activities of all components are one).

Eq. (7.427) is called the Nernst equation and is usually written as (Q = reaction quotient):

$$E = E^\circ - \frac{RT}{|v_e|F} \ln \left(\prod_{i=1}^{N_s} a_i^{v_s} \right) \stackrel{\text{Eq. (5.303)}}{=} E^\circ - \frac{RT}{|v_e|F} \ln(Q) \quad (7.428)$$

At 25 °C this can be written:

$$E = E^\circ - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{|v_e|(96485 \text{ C mol}^{-1})} \ln(Q) = E^\circ - \frac{0.02569}{|v_e|} \ln(Q) \quad (7.429)$$

At equilibrium no electrons flow between the electrodes (i.e. $E = 0$) and we have:

$$E^\circ = \frac{RT}{|v_e|F} \ln(K) \text{ or } K = \exp \left(\frac{|v_e|FE^\circ}{RT} \right) \quad (7.430)$$

where K is the equilibrium constant for the cell reaction.

Example. Three different galvanic cells have standard EMFs E° of 0.01, 0.1 and 1.0 V at 25 °C. Calculate the equilibrium constants of the reactions that occur in these cells assuming the charge number $|v_e|$ for each reaction is unity.

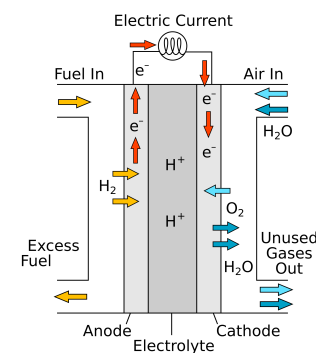
Solution. Use Eq. (7.430) to get the equilibrium constants:

$$K(0.01 \text{ V}) = \exp \left(\frac{(96485 \text{ C mol}^{-1})(0.01 \text{ V})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} \right) = 1.476$$

$$K(0.1 \text{ V}) = 49.0$$

$$K(1.0 \text{ V}) = 8.02 \times 10^{16}$$

Example. Fuel cell is an electrochemical cell, which typically uses O_2 and H_2 gas to produce electricity. Note that this approach provides higher efficiency than just a simple combustion process involving O_2/H_2 where the heat release reduces the amount of work obtainable from the system (the first law of thermodynamics).



7.4 Activity of electrolytes

Electrolytes have to be treated in a different way from nonelectrolytes because they dissociate. However, the ions cannot be studied separately because the condition of electric neutrality applies.

For electrolyte solutions, it is customary to use the molal scale (instead of molar). The unit of molality is mol kg^{-1} (for molarity mol L^{-1}). Conversion between the systems can be carried out by multiplication / division by the solvent density (kg L^{-1}). Note that molality does not change as a function of temperature whereas molarity usually does.

On the molality scale, the activity of a solute is given by (compare with Eq. (6.386)):

$$a_i = \frac{\gamma_i m_i}{m^\circ} \quad (7.431)$$

where a_i denotes activity, γ_i activity coefficient, m_i molality and m° standard molality (1 mol / kg of solvent). For dilute solutions we have:

$$\lim_{m_i \rightarrow 0} \gamma_i = 1 \quad (7.432)$$

Addition of an infinitely small amount of an electrolyte to one kg of solvent, yields a small change in the Gibbs energy:

$$dG = \mu_+ dm_+ + \mu_- dm_- \quad (7.433)$$

Note that we cannot add cations or anions separately, we always get both when an electrolyte is added to the solvent.

<i>Electrolyte</i>	Substance that dissolves to give an ionically conducting solution.
<i>Non-electrolyte</i>	Substance that dissolves to give a solution that does not conduct electricity.
<i>Strong electrolyte</i>	Substance that dissolves completely, or almost completely to give an ionically conducting solution.
<i>Weak electrolyte</i>	Substance that dissolves only to a small degree.

Consider a strong electrolyte $A_{v_+}B_{v_-}$ where v_+ is the number of cations and v_- is the number of anions. The overall electroneutrality condition for the solution gives:

$$m = \frac{m_+}{v_+} = \frac{m_-}{v_-} \quad (7.434)$$

Inserting this into Eq. (7.433) gives:

$$dG = (v_+ \mu_+ + v_- \mu_-) dm = \mu dm \quad (7.435)$$

where $\mu = v_+ \mu_+ + v_- \mu_-$

Here μ is the chemical potential for the electrolyte, which can be determined experimentally.

Note: In the following we will omit the standard state value m° from expressions. This results in simplified expressions but it will give inconsistent units! For example, m_i/m° becomes now just m_i .

The chemical potentials for cation and anion are given by:

$$\mu_+ = \mu_+^\circ + RT \ln(\gamma_+ m_+) \quad (\mu_+^\circ \text{ std state chemical potential for cation}) \quad (7.436)$$

$$\mu_- = \mu_-^\circ + RT \ln(\gamma_- m_-) \quad (\mu_-^\circ \text{ std state chemical potential for anion}) \quad (7.437)$$

Combining Eqs. (7.436) and (7.437) gives:

$$\mu = (v_+ \mu_+^\circ + v_- \mu_-^\circ) + RT \ln(\gamma_+^{v_+} \gamma_-^{v_-} m_+^{v_+} m_-^{v_-}) \quad (7.438)$$

To make the logarithm argument proportional to m , we define the mean ionic molality m_\pm and the mean ionic activity coefficient γ_\pm (with help of Eq. (7.434)):

$$m_\pm = (m_+^{v_+} m_-^{v_-})^{1/v_\pm} = m (v_+^{v_+} v_-^{v_-})^{1/v_\pm} \quad (7.439)$$

$$\gamma_\pm = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/v_\pm} \quad (7.440)$$

$$v_\pm = v_+ + v_- \quad (7.441)$$

Using these definitions we can rewrite Eq. (7.438) as:

$$\mu = \mu^\circ + v_\pm RT \ln(\gamma_\pm m_\pm) \quad (7.442)$$

$$\text{with } a_{A_{v_+} B_{v_-}} = (\gamma_\pm m_\pm)^{v_\pm} = \gamma_\pm^{v_\pm} m^{v_\pm} (v_+^{v_+} v_-^{v_-})$$

where $A_{v_+} B_{v_-}$ is the electrolyte activity. The standard chemical potential μ° of the electrolyte is the chemical potential in a solution of unit activity on the molality scale.

Examples. What are the mean ionic molalities m_\pm of NaCl, CaCl₂, CuSO₄ and LaCl₃?

Solution. NaCl: 1 - 1 electrolyte and hence Eq. (7.439) gives $m_\pm = m$. Here m is the molality of the electrolyte.

CaCl₂: 1 - 2 electrolyte and hence Eq. (7.439) gives $m_\pm = 4^{1/3} m$.

CuSO₄: 1 - 1 electrolyte and hence Eq. (7.439) gives $m_\pm = m$.

LaCl₃: 1 - 3 electrolyte and hence Eq. (7.439) gives $m_\pm = 27^{1/4} m$.

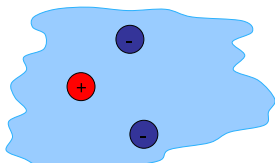
7.5 Debye-Hückel theory

Electrolytes containing multiply charged ions (for example, Cu^{2+}) have greater effect on the activity constants of ions than singly charged ions (for example, H^+). To account for this, we define ionic strength I (G. N. Lewis):

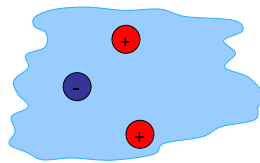
$$I = \frac{1}{2} \sum_{i=1}^{N_s} m_i z_i^2 = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + \dots + m_{N_s} z_{N_s}^2) \quad (7.443)$$

where m_i is molality of ion i and z_i is charge for ion i in units of $|e|$ (signed quantity).

Why is the activity of ions reduced in a solution?



On average "+" has more negative charges around. This shields "+" and reduces its activity.



On average "-" has more positive charges around. This shields "-" and reduces its activity.

Note that because the Coulomb interaction has long range, it is nearly impossible to prepare dilute electrolytic solutions.

315

In 1923 Peter Debye and Erich Hückel were able to show that for dilute solutions the activity coefficient γ_i of ion i with a charge number z_i is given by (for details, see Phys. Z. 24:185, 305 (1923)):

$$\log(\gamma_i) = -A z_i^2 \sqrt{I} \quad (7.444)$$

where I is the ionic strength given by Eq. (7.443) and:

$$A = \frac{1}{2.303} \left(\frac{2\pi N_A m_{\text{sol}}}{V} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r kT} \right)^{3/2} \quad (7.445)$$

Here m_{sol} is the mass of solvent in volume V and ϵ_r is the relative permittivity of the solvent, N_A is Avogadro's number (6.022137×10^{23} molecules / mol), e is the electron charge ($1.6021773 \times 10^{-19}$ C), ϵ_0 is the vacuum permittivity ($8.8541878 \times 10^{-12}$ As V $^{-1}$ m $^{-1}$).

To take the mean of ion activities, we first take logarithm of Eq. (7.440):

$$\log(\gamma_{\pm}) = \frac{1}{v_+ + v_-} (v_+ \log(\gamma_+) + v_- \log(\gamma_-)) \quad (7.446)$$

Substitution of Eq. (7.444) into (7.446) gives:

$$\log(\gamma_{\pm}) = -A \left(\frac{v_+ z_+^2 + v_- z_-^2}{v_+ + v_-} \right) \sqrt{I} \quad (7.447)$$



Peter Debye, Dutch chemist (1884 - 1966), Nobel prize 1936.



Erich Hückel, German chemist (1896 - 1980).

By using the total charge neutrality $v_+z_+ = -v_-z_-$, we get:

$$\log(\gamma_{\pm}) = Az_+z_-\sqrt{I} \quad (7.448)$$

where z has the sign corresponding to the ion.

Example. Use the Debye-Hückel theory to calculate γ_+ , γ_- , γ_{\pm} and a_{NaCl} for 0.001 molal sodium chloride in water at 25 °C. Density of water is about 0.997 kg L⁻¹. The relative permittivity of H₂O at this temperature is 78.54.

Solution. Eqs. (7.443), (7.444) and (7.445) give:

$$\begin{aligned} A &= \frac{1}{2.303} \left(\frac{2\pi N_A m_{\text{solv}}}{V} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r kT} \right)^{3/2} \\ &= \frac{1}{2.303} \left(\frac{2\pi (6.022 \times 10^{23} \text{ mol}^{-1}) (997 \text{ kg})}{(1.000 \text{ m}^3)} \right)^{1/2} \\ &\quad \times \left(\frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi (8.854 \times 10^{-12} \text{ AsV}^{-1}\text{m}^{-1}) (78.54) (1.3861 \times 10^{-23} \text{ JK}^{-1}) (298.2 \text{ K})} \right)^{3/2} \\ &= 0.509 \text{ kg}^{1/2}\text{mol}^{-1/2} \end{aligned}$$

$$I = \frac{1}{2} \left((0.001 \text{ mol kg}^{-1}) \times (-1)^2 + (0.001 \text{ mol kg}^{-1}) \times (1)^2 \right) = 0.001 \text{ mol kg}^{-1}$$

$$\log(\gamma_+) = \log(\gamma_-) = -Az_+^2\sqrt{I} = -Az_-^2\sqrt{I} = - (0.509 \text{ kg}^{1/2}\text{mol}^{-1/2}) \times (\pm 1)^2$$

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ ↺ ↻ ↻

$$\times \sqrt{0.001 \text{ mol kg}^{-1}} = -1.610 \times 10^{-2} \Rightarrow \gamma_+ = \gamma_- = 0.964$$

Next Eq. (7.448) yields:

$$\begin{aligned} \log(\gamma_{\pm}) &= Az_+z_-\sqrt{I} = (0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}) \times (1) \times (-1) \times (0.001)^{1/2} \\ &\Rightarrow \gamma_{\pm} = (\gamma_+\gamma_-)^{1/2} = 0.964 \\ a_{\text{NaCl}} &= m^2\gamma_{\pm}^2 = (0.001^2)(0.964)^2 = 9.29 \times 10^{-7} \end{aligned}$$

Note: The Debye-Hückel law, Eq (7.444), works well up to ionic strengths about 0.01. However, large deviations between experiment and Eq. (7.444) are observed already at this ionic strength when ions have high charges (greater than 4). This is because Eq. (7.444) is an approximate result.

At high ionic strengths the following empirical relation is often useful (extended Debye-Hückel equation):

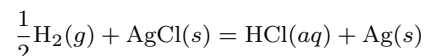
$$\begin{aligned} \log(\gamma_{\pm}) &= \frac{Az_+z_-\sqrt{I}}{1 + B\sqrt{I}} \\ \text{or } \log(\gamma_i) &= \frac{Az_i^2\sqrt{I}}{1 + B\sqrt{I}} \end{aligned} \quad (7.449)$$

where $B = 1.6 \text{ kg}^{1/2}\text{mol}^{-1/2}$ at 25 °C.

◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ ↺ ↻ ↻

Determination of activity coefficients using an electrochemical cell:

Consider the following reaction:



The charge number in this reaction is one and the EMF is given by Eq. (7.428):

$$E = E^\circ - \frac{RT}{F} \ln \left(\frac{a_{\text{HCl}}}{\sqrt{P_{\text{H}_2}/P^\circ}} \right) \quad (7.450)$$

where we have assumed H_2 to be an ideal gas. If the pressure of hydrogen is 1 bar and Eq. (7.442) is introduced, we get:

$$E = E^\circ - \frac{2.303RT}{F} \log(\gamma_{\pm}^2 m^2) = E^\circ - 0.05916 \log(\gamma_{\pm}^2 m^2) \quad (7.451)$$

where γ_{\pm} is the HCl mean ionic activity and m is HCl molality. The last step was obtained at 25 °C.

Eq. (7.451) contains two unknowns, but they can be determined from a series measurements of the cell EMF with different HCl molalities. Rearranging Eq. (7.451) gives:

$$E + 0.1183 \log(m) = E^\circ - 0.1183 \log(\gamma_{\pm}) \quad (7.452)$$

Plotting $E + 0.1183 \log(m)$ against m and extrapolating to infinitely dilute HCl solution (i.e., $m \rightarrow 0$ and $\gamma_{\pm} \rightarrow 1$) gives an experimental estimate for E° . This equation can be combined with the extended Debye-Hückel law to give better results at higher ionic strengths. After determining E° , Eq. (7.452) can be directly used to obtain γ_{\pm} .

Table. Mean ionic activity coefficients γ_{\pm} in water at 25 °C.

m (mol kg ⁻¹)	HCl	LiCl	NaCl	CsCl
0.01	0.905	0.904	0.902	0.899
0.02	0.875	0.873	0.870	0.865
0.05	0.830	0.825	0.820	0.807
0.10	0.796	0.790	0.778	0.756
0.20	0.767	0.757	0.735	0.718
0.40	0.755	0.740	0.693	0.628
1.0	0.809	0.774	0.657	0.544
2.0	1.009	0.921	0.668	0.495
3.0	1.316	1.156	0.714	0.478
4.0	1.762	1.510	0.783	0.473
5.0	2.38	2.02	0.874	0.474

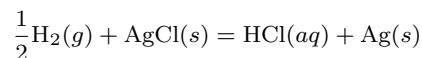
In general, if activity coefficient is greater than one, positive deviation from Raoult's law occurs (A-A/B-B interaction stronger than A-B), otherwise negative deviation occurs (A-B stronger than A-A/B-B).

7.6 Determination of standard thermodynamic properties of ions

According to Eq. (7.430) the standard EMF (E°) can be determined from:

$$\Delta_r G^\circ = -|v_e| F E^\circ = -RT \ln(K) \quad (7.453)$$

If we consider reaction:



The equilibrium constant for this reaction is given by:

$$K = \exp \left(\frac{(96485 \text{ C mol}^{-1}) (0.2224 \text{ V})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})} \right) = 5745 \quad (7.454)$$

$$K = \frac{a_{\text{HCl}}}{\sqrt{P_{\text{H}_2}/P^\circ}} \quad (\text{H}_2 \text{ ideal gas})$$

If the standard EMF of a cell is measured as a function of temperature, then $\Delta_r S^\circ$, $\Delta_r H^\circ$ and $\Delta_r C_P^\circ$ can be calculated using the following relations (see Eqs. (2.112), (4.221), $H = G + TS$, and (7.453)):

$$\Delta_r S^\circ = |v_e| F \left(\frac{\partial E^\circ}{\partial T} \right)_P \quad (7.455)$$

$$\Delta_r H^\circ = -|v_e| F E^\circ + |v_e| F T \left(\frac{\partial E^\circ}{\partial T} \right)_P \quad (7.456)$$

$$\Delta_r C_P^\circ = |v_e| F T \left(\frac{\partial^2 E^\circ}{\partial T^2} \right)_P \quad (7.457)$$

Notes:

1. These standard thermodynamic properties have been expressed with respect to a hypothetical standard state where the electrolyte has molality of 1 mol kg⁻¹ and the interactions for the resulting ions correspond to infinite dilution. For example, the true activity of 1 mol kg⁻¹ HCl solution is less than 1.
2. The standard thermodynamic properties have been tabulated (see the NIST online database). The standard state for strong electrolytes is assumed to consists of completely ionized (for example, HCl, NaCl, etc.). For weak electrolytes, usually two different standard states are given: fully ionized and un-ionized (not dissociated).
3. The experiments can not measure individual ions separately (electroneutrality condition). However, by using a convention: $\Delta_f G^\circ(\text{H}^+) = \Delta_f H^\circ(\text{H}^+) = 0$, the properties of other ions can be calculated.
4. For strong electrolytes the standard Gibbs energy of formation can be obtained by summing the corresponding formation energies for the ions.

Example. Calculate the standard molar entropy of chloride ion in aqueous solution at 298.15 K starting with the Gibbs energy of formation ($-131.23 \text{ kJ mol}^{-1}$) and the enthalpy of formation ($-167.16 \text{ kJ mol}^{-1}$). $\bar{S}^\circ(\text{H}_2(g)) = 130.68 \text{ J/(K mol)}$ and $\bar{S}^\circ = 223.07 \text{ J/(K mol)}$.

Solution. By using " $G = H - TS$ " we can calculate $\Delta_f S^\circ$:

$$\begin{aligned}\Delta_f S^\circ(\text{Cl}^-) &= \frac{\Delta_f H^\circ(\text{Cl}^-) - \Delta_f G^\circ(\text{Cl}^-)}{T} = \frac{(-167.16 \text{ kJ mol}^{-1}) - (-131.23 \text{ kJ mol}^{-1})}{298.15 \text{ K}} \\ &= -120.51 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Consider the following reaction: $\frac{1}{2}\text{Cl}_2(g) + e^- = \text{Cl}^-(aq)$

Now we can write: $\Delta_f \bar{S}^\circ(\text{Cl}^-) = \bar{S}^\circ(\text{Cl}^-) - \frac{1}{2}\bar{S}^\circ(\text{Cl}_2) - \bar{S}^\circ(e^-)$

where $\bar{S}^\circ(e^-) = 1/2 \times \bar{S}^\circ(\text{H}_2(g))$ because $2e^- + 2\text{H}^+ = \text{H}_2$. Thus we can write:

$$\begin{aligned}\bar{S}^\circ(\text{Cl}^-) &= \Delta_f \bar{S}^\circ(\text{Cl}^-) + \frac{1}{2}\bar{S}^\circ(\text{Cl}_2) + \bar{S}^\circ(e^-) = (-120.51 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &+ \left(\frac{(223.08 \text{ J K}^{-1} \text{ mol}^{-1})}{2} \right) + \left(\frac{(130.68 \text{ J K}^{-1} \text{ mol}^{-1})}{2} \right) = 56.36 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

It should be remembered that the tabulated data (e.g. the NIST database) gives the properties in the limit of zero ionic strength. At higher ionic strengths the extended Debye-Hückel law must be used. Some quantitative expressions are as follows:

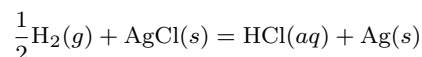
$$\Delta_f G_i^\circ(I) = \Delta_f G_i^\circ(I \rightarrow 0) - RT \ln(\gamma_i) \quad (7.458)$$

$$\Delta_f H^\circ(I) = -T^2 \left[\frac{\partial (\Delta_f G_i^\circ(I)/T)}{\partial T} \right]_P \quad (7.459)$$

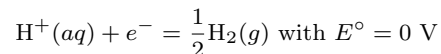
$\Delta_r G^\circ$ and $\Delta_r H^\circ$ can be obtained by using the above expressions and Eqs. (2.139) and (5.321).

7.7 Standard electrode potentials

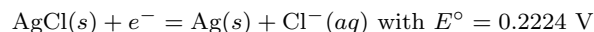
Standard electrode potentials can be used to calculate the EMF of a given electrochemical cell. The standard electrode potential of a cell can be obtained with hydrogen electrode on the left and all components at unit activity. For example:



which can be measured to be 0.2224 V. Also the hydrogen electrode contribution is taken to be (arbitrarily) zero:



Thus the only contribution to the cell potential is only from the reaction:



Note that these reactions are written as reduction reactions and therefore E° can also be called reduction potential. A brief listing of various standard electrode potentials are given in the following table:

325

Table. Standard electrode potentials at 25 °C.

Electrode	E° (V)	Electrode reaction
$\text{F}^- \text{F}_2(g) \text{Pt}$	2.87	$(1/2) \text{F}_2(g) + e^- = \text{F}^-$
$\text{Au}^{3+} \text{Au}$	1.50	$(1/3) \text{Au}^{3+} + e^- = \text{Au}$
$\text{Pb}^{2+} \text{PbO}_2 \text{Pb}$	1.455	$(1/2) \text{PbO}_2 + 2\text{H}^+ + e^- = (1/2)\text{Pb}^{2+} + \text{H}_2\text{O}$
$\text{Cl}^- \text{Cl}_2(g) \text{Pt}$	1.3604	$(1/2) \text{Cl}_2(g) + e^- = \text{Cl}^-$
$\text{H}^+ \text{O}_2(g) \text{Pt}$	1.2288	$\text{H}^+ + (1/4)\text{O}_2(g) + e^- = (1/2)\text{H}_2\text{O}$
$\text{Ag}^+ \text{Ag}$	0.7992	$\text{Ag}^+ + e^- = \text{Ag}$
$\text{Fe}^{3+}, \text{Fe}^{2+} \text{Pt}$	0.771	$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$
$\text{I}^- \text{I}_2(s) \text{Pt}$	0.5355	$(1/2)\text{I}_2 + e^- = \text{I}^-$
$\text{Cu}^+ \text{Cu}$	0.521	$\text{Cu}^+ + e^- = \text{Cu}$
$\text{OH}^- \text{O}_2(g) \text{Pt}$	0.4009	$(1/4) \text{O}_2(g) + (1/2)\text{H}_2\text{O} + e^- = \text{OH}^-$
$\text{Cu}^{2+} \text{Cu}$	0.3394	$(1/2) \text{Cu}^{2+} + e^- = (1/2)\text{Cu}^+$
$\text{Cl}^- \text{Hg}_2\text{Cl}_2(s) \text{Hg}$	0.268	$(1/2) \text{Hg}_2\text{Cl}_2 + e^- = \text{Hg} + \text{Cl}^-$
$\text{Cl}^- \text{AgCl}(s) \text{Ag}$	0.2224	$\text{AgCl} + e^- = \text{Ag} + \text{Cl}^-$
$\text{Cu}^{2+}, \text{Cu}^+ \text{Pt}$	0.153	$\text{Cu}^{2+} + e^- = \text{Cu}^+$
$\text{Br}^- \text{AgBr}(s) \text{Ag}$	0.0732	$\text{AgBr} + e^- = \text{Ag} + \text{Br}^-$
$\text{H}^+ \text{H}_2(g) \text{Pt}$	0.0000	$\text{H}^+ + e^- = (1/2)\text{H}_2$
$\text{D}^+ \text{D}_2(g) \text{Pt}$	-0.0034	$\text{D}^+ + e^- = (1/2)\text{D}_2$
$\text{Pb}^{2+} \text{Pb}$	-0.126	$(1/2) \text{Pb}^{2+} + e^- = (1/2)\text{Pb}$
$\text{Sn}^{2+} \text{Sn}$	-0.140	$(1/2) \text{Sn}^{2+} + e^- = (1/2)\text{Sn}$
$\text{Ni}^{2+} \text{Ni}$	-0.250	$(1/2) \text{Ni}^{2+} + e^- = (1/2)\text{Ni}$
$\text{Cd}^{2+} \text{Cd}$	-0.4022	$(1/2) \text{Cd}^{2+} + e^- = (1/2)\text{Cd}$
$\text{Fe}^{2+} \text{Fe}$	-0.440	$(1/2) \text{Fe}^{2+} + e^- = (1/2)\text{Fe}$
$\text{Zn}^{2+} \text{Zn}$	-0.763	$(1/2) \text{Zn}^{2+} + e^- = (1/2)\text{Zn}$
$\text{OH}^- \text{H}_2(g) \text{Pt}$	-0.8279	$\text{H}_2\text{O} + e^- = (1/2)\text{H}_2(g) + \text{OH}^-$
$\text{Mg}^{2+} \text{Mg}$	-2.37	$(1/2) \text{Mg}^{2+} + e^- = (1/2)\text{Mg}$
$\text{Na}^+ \text{Na}$	-2.714	$\text{Na}^+ + e^- = \text{Na}$
$\text{Li}^+ \text{Li}$	-3.045	$\text{Li}^+ + e^- = \text{Li}$

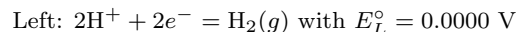
The cell EMF E can now be expressed as a difference between the right and left electrode potentials:

$$E = E_R - E_L \text{ and } E^\circ = E_R^\circ - E_L^\circ \quad (7.460)$$

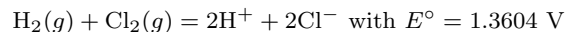
Note that given the data in the previous table, it is now possible to use the Nernst Eq. (7.428) to obtain E for a cell when the concentrations or partial pressures are given. Furthermore, the table data indicates the polarities for the electrodes and can be used for obtaining the equilibrium constants (K) via Eq. (7.430).

Rules for using the table data:

1. The half-cell reactions are written as reduction reactions. Consider, for example, a cell consisting of $\text{Pt} \mid \text{H}_2(g) \mid \text{HCl}(aq) \mid \text{Cl}_2(g) \mid \text{Pt}$. The half-cell reactions are:



2. Both reactions must be written with the same number of electrons. Note that E° does not depend on $|v_e|$.
3. The standard EMF for the cell (E°) is obtained by using Eq. (7.460). In the above example this gives $E^\circ = 1.3604 \text{ V} - 0.0000 \text{ V} = 1.3604 \text{ V}$. The overall reactions is:

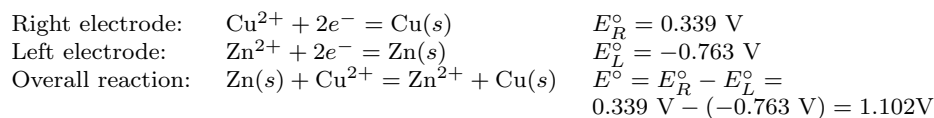


4. If, under the standard condition, the standard EMF is positive, the reaction will spontaneously go from left to right. In this case the right electrode is positive (+) and the left electrode negative (−) when the cell is operated as a galvanic cell.
5. If, under the standard condition, the standard EMF is negative, the reaction will spontaneously go from right to left. In this case the right electrode is negative (−) and the left electrode positive (+) when the cell is operated as an electrolytic cell.
6. The equilibrium constant for the cell can be obtained by using Eq. (7.430).
7. The cell EMF under non-standard condition can be obtained by using the Nernst equation (Eq. (7.428)). Note that if the cell has a liquid junction, the Nernst equation must be written in terms of ion species (see the following example).

Example. Consider the following galvanic cell: $\text{Zn}(s) \mid \text{Zn}^{2+} :: \text{Cu}^{2+} \mid \text{Cu}(s)$ where $::$ denotes a liquid junction ($T = 298.15 \text{ K}$). Assume that Cu^{2+} and Zn^{2+} have identical ionic strengths on both sides of the liquid junction.

- (a) What is the cell reaction?
- (b) What is the standard EMF for the cell?
- (c) What is the value of the equilibrium constant?
- (d) What is the expression for the equilibrium constant in terms of ion concentrations?

Solution. Parts a) and b). The electrode reactions are:



Thus Zn is oxidized (left) and Cu^{2+} is reduced (right).

Part c.

Eq. (7.430) gives:

$$K = \exp\left(\frac{|v_e| F E^\circ}{RT}\right) = \exp\left(\frac{2 (96485 \text{ C mol}^{-1}) (1.102 \text{ V})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})}\right) = 1.80 \times 10^{37}$$

Part d. Solids have activities of one and hence (using Eqs. (7.431) and (7.444)):

$$K = \frac{a(\text{Zn}^{2+}) a(\text{Cu}(s))}{a(\text{Cu}^{2+}) a(\text{Zn}(s))} = \frac{a(\text{Zn}^{2+})}{a(\text{Cu}^{2+})} = \frac{\gamma(\text{Zn}^{2+}) m(\text{Zn}^{2+})}{\gamma(\text{Cu}^{2+}) m(\text{Cu}^{2+})} \approx \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Example. Demonstrate with the $\text{Cu}/\text{Cu}^+/\text{Cu}^{2+}$ sequence that the value for E° for the reaction $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ ($E_1^\circ = +0.339 \text{ V}$; reaction #1) cannot be obtained simply by summing the E° values from reactions $\text{Cu}^+ + e^- \rightarrow \text{Cu}$ ($E_2^\circ = +0.521 \text{ V}$; reaction #2) and $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$ ($E_3^\circ = +0.153 \text{ V}$; reaction #3).

Solution. The correct way to proceed is to consider the standard reaction Gibbs energies ($\Delta_r G^\circ$):

Reaction 1 ($ v_e = 2$):	$\Delta_r G_1^\circ = - v_e F E^\circ = -0.678 \times F$
Reaction 2 ($ v_e = 1$):	$\Delta_r G_2^\circ = - v_e F E^\circ = -0.521 \times F$
Reaction 3 ($ v_e = 1$):	$\Delta_r G_3^\circ = - v_e F E^\circ = -0.153 \times F$

Thus $\Delta_r G_1^\circ = \Delta_r G_2^\circ + \Delta_r G_3^\circ$ but $E_1^\circ \neq E_2^\circ + E_3^\circ$.

Notes:

1. If the solvent is involved in the reaction, the solvent is usually treated on the mole fraction scale rather than the molal (or molar) scale. In this case the equilibrium constant expression can be written as:

$$K = (\gamma_{x,A} x_A)^{v_A} \prod_{i \neq A} \left(\frac{\gamma_{m,i} m_i}{m^\circ} \right)^{v_i} \quad (7.461)$$

where A denotes the solvent, $\gamma_{x,A}$ is its activity coefficient on the mole fraction scale, $\gamma_{m,i}$ is the activity coefficient of reactant i on the molal scale and m° is the standard state molality (1 mol kg⁻¹). For dilute solutions Eq. (7.461) can be written approximately as:

$$K = \prod_{i \neq A} \left(\frac{\gamma_{m,i} m_i}{m^\circ} \right)^{v_i} \quad (7.462)$$

Even though the solvent is left out from the equation, the Gibbs energy of formation of the solvent must be included in calculating $\Delta_r G^\circ$ for the reaction.

2. Some species in aqueous solution may be listed in thermodynamic tables in more than one way. For example, NH₃ vs. NH₄OH or CO₂ vs. H₂CO₃. In many cases we don't know the extent of hydration because of the difficulty in distinguishing the species in solution. The convention in the NBS tables is that $\Delta_f G^\circ = \Delta_f H^\circ = \Delta_f S^\circ = 0$ for hydration reactions $B + nH_2O = B(H_2O)_n$ where B denotes the species in question. This means that either one of the pair can be used in the calculations.

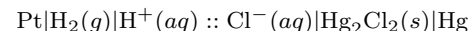
7.8 Determination of pH

The concentrations of hydrogen ions (H⁺) in aqueous solutions (in form of H₃O⁺) range from about 1 mol L⁻¹ (1 M HCl) to about 10⁻¹⁴ mol L⁻¹ (1 M NaOH). Because of the wide range of concentrations an exponential scale is used (Søren Sørensen, Danish biochemist, 1868 – 1939). The exponential scale is defined (pH scale):

$$pH = -\log (a_{H^+}) \quad (7.463)$$

Strictly speaking, the activity of a single ion cannot be determined, but pH meters are calibrated with buffers for which the pH has been calculated using the extended Debye-Hückel equation (Eq. (7.449)).

pH may be measured with a hydrogen electrode connected with a calomel electrode through a salt bridge:



Often the contribution of the liquid junction is negligible to the cell EMF and we can calculate E° for the cell (0.2802 V at 25 °C) and use the Nernst equation (Eq. (7.428) and assuming that H₂ is an ideal gas):

$$\begin{aligned} E &= E^\circ - \frac{RT}{|v_e| F} \ln \left(\frac{a(\text{H}^+)}{a(\text{H}_2(g))} \right) = E^\circ - 2.303 \times \underbrace{\frac{0.02569 \text{ V}}{|v_e| F}}_{=1} \log \left(\frac{a(\text{H}^+)}{a(\text{H}_2(g))} \right) \quad (7.464) \\ &= E^\circ - (0.0591 \text{ V}) \log \left(\frac{a(\text{H}^+)}{P(\text{H}_2)/P^\circ} \right) = E^\circ - (0.0591 \text{ V}) \log (a(\text{H}^+)) \end{aligned}$$

8.1 Introduction to statistical thermodynamics

The statistical ensemble

- ▶ Theory developed by Maxwell, Boltzmann, Gibbs and Einstein between 1860 - 1905.
- ▶ Offers microscopic view to thermodynamics.
- ▶ Provides a natural connection between thermodynamics and quantum mechanics. The latter has not yet been covered.
- ▶ Quantum mechanics provides a way to calculate energies of microsystems (electronic, translational, vibrational, rotational), which are denoted by E_i below.

Terminology:

System	= Macroscopic thermodynamic system.
Particles	= Fundamental particles that compose the system.
Macrostate	= Macroscopic parameters (e.g., V, P, T) specifying the system.
Microstate	= Atom/molecular level specification of the system. These would correspond to coordinates and velocities of atoms/molecules, for example.

Note: For a given macrostate, many different microstates are possible. Usually only macrostates are observable.

Ensemble: A hypothetical collection of non-interacting systems, each of which is in the same *macrostate* as the system of interest. Although the members of the ensemble are macroscopically identical, they may not be in the same *microstate*.

Measurement: A measurement of any macroscopic property consists of a time average over the measurement interval. Hence it involves an inherent time averaging process.

Postulate: The measured time average of any macroscopic property of the system is equal to the average value of that property in the ensemble. Note that this replaces the need to use time averages in the calculations.

An ensemble of systems that all have constant macroscopic parameters T and V is called *canonical ensemble*.

The internal energy of a macroscopic system is given as an ensemble average:

$$U = \langle E_i \rangle = \sum_{i=1}^{\infty} p_i E_i \quad (8.467)$$

where $\langle \rangle$ denotes the ensemble average, E_i is the energy of system i and p_i is the statistical weight for state i (i.e., probability of state i).

We will show that the statistical weights p_i are given by the Boltzmann probability:

$$p_i = \frac{e^{-\beta E_i}}{Z} \quad (8.468)$$

where Z is the canonical partition function (do not confuse this with the compressibility factor which was also denoted by Z earlier), which is defined as:

$$Z = \sum_{i=1}^{\infty} e^{-\beta E_i} \quad (8.469)$$

Assumption: For a thermodynamic system at fixed $V, \{n_i\}, T$, all microstates that have equal energy have equal probability of occurring. This implies that $p_i = f(E_i)$ (i.e. the statistical weights depend only on the microstate energy). Note that the above Boltzmann probability is consistent with this postulate.

In the following, we will derive the Boltzmann probabilities and expressions for U, P and S . We will also show that β is a function of temperature only and has the form $\beta = \frac{1}{kT}$ where k is the Boltzmann constant.

Evaluation of p_i (the Boltzmann probabilities):

We need to determine the unknown function f in the above postulate. Consider two subsystems, which are labeled 1 and 2, in an ensemble. All ensemble members labeled 1 are macroscopically identical and all members of 2 are macroscopically identical. However, 1 and 2 are not necessarily identical as they can differ in volume V and composition $\{n_i\}$. For 1 and 2 we then have:

$$p_{1,i} = f(E_{1,i}) \text{ and } p_{2,j} = g(E_{2,j}) \quad (8.470)$$

where $p_{1,i}$ is the probability for system 1 to be in microstate i (energy $E_{1,i}$) and $p_{2,j}$ for system 2 to be in microstate j (energy $E_{2,j}$). Note that f and g are not necessarily the same functions. Systems 1 and 2 can also be considered as a combined single system with overall fixed volume, temperature and composition:

$$p_{1+2,k} = h(E_{1+2,k}) \quad (8.471)$$

where $p_{1+2,k}$ is the probability that system 1+2 is in microstate k . Since systems 1 and 2 are independent of each other, we have:

$$E_{1+2,k} = E_{1,i} + E_{2,j} \text{ with } k = (i, j) \quad (8.472)$$

Furthermore since the systems 1 and 2 are independent, their overall probability is given as a product:

339

$$h(E_{1+2,k}) = h(E_{1,i} + E_{2,j}) = f(E_{1,i})g(E_{2,j}) \quad (8.473)$$

With $x \equiv E_{1,i}$, $y \equiv E_{2,j}$ and $z \equiv x + y$ we can rewrite the above equation as:

$$h(z) = f(x)g(y) \quad (8.474)$$

Differentiation of this equation gives:

$$\left(\frac{\partial h(z)}{\partial x} \right)_y = \left(\frac{df(x)}{dx} \right) g(y) \quad (8.475)$$

By using the chain rule we get:

$$\left(\frac{\partial h(z)}{\partial x} \right)_y = \left(\frac{dh(z)}{dz} \right) \left(\frac{\partial z}{\partial x} \right)_y = \frac{dh(z)}{dz} \quad (8.476)$$

Combining Eqs. (8.475) and (8.476) gives:

$$\frac{dh(z)}{dz} = \frac{df(x)}{dx} g(y) \quad (8.477)$$

In similar way, differentiation with respect to y gives:

$$\frac{dh(z)}{dz} = f(x) \frac{dg(y)}{dy} \quad (8.478)$$

By combining Eqs. (8.477) and (8.478) we get:

$$\frac{g'(y)}{g(y)} = \frac{f'(x)}{f(x)} \equiv -\beta \text{ (constant)} \quad (8.479)$$

For f this gives the following differential equation:

$$\begin{aligned} f'(x) &= -\beta f(x) \Rightarrow f(x) = C e^{-\beta x} \\ \Rightarrow f(x) &= C e^{-\beta E_{1,i}} \end{aligned} \quad (8.480)$$

where C is a constant of integration and β is a universal constant that is the same for both systems 1 and 2. Note that β may depend on temperature. The normalization constant C has to be chosen such that the sum over probabilities gives unity:

$$\sum_{i=1}^{\infty} C e^{-\beta E_{1,i}} = 1 \Rightarrow C = \frac{1}{\sum_{i=1}^{\infty} e^{-\beta E_{1,i}}} \equiv \frac{1}{Z} \quad (8.481)$$

Thus the probabilities are given by:

$$p_i = \frac{e^{-\beta E_i}}{\sum_{j=1}^{\infty} e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Z} \quad (8.482)$$

We will later derive the exact form for β .

Evaluation of U and P :

$$U = \sum_{i=1}^{\infty} p_i E_i = \frac{\sum_{i=1}^{\infty} E_i e^{-\beta E_i}}{Z} \quad (8.483)$$

where $Z = Z(\beta(T), V, \{n_i\})$. Differentiation of Z with respect to β gives:

$$\left(\frac{\partial Z}{\partial \beta} \right)_{V, \{n_i\}} = \left(\frac{\partial}{\partial \beta} \right)_{V, \{n_i\}} \sum_{j=1}^{\infty} e^{-\beta E_j} = - \sum_{j=1}^{\infty} E_j e^{-\beta E_j} \quad (8.484)$$

Now Eq. (8.483) can finally be written as:

$$U = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)_{V, \{n_i\}} = - \left(\frac{\partial \ln(Z)}{\partial \beta} \right)_{V, \{n_i\}} \quad (8.485)$$

Consider next the measurement of pressure P :

$$P = \sum_{i=1}^{\infty} p_i P_i \quad (8.486)$$

where P_i is the pressure in the i th member of the ensemble. If we have non-interacting and adiabatic systems, we can write the internal energy differential in two ways (for each member of the ensemble):

$$dU = dw_{rev} = -P_i dV \quad (8.487)$$

$$dU = \left(\frac{\partial E_i}{\partial V} \right) dV \quad (\text{total differential})$$

$$\Rightarrow P_i = - \left(\frac{\partial E_i}{\partial V} \right)$$

where E_i is the energy of ensemble member i . This gives an expression for the measured pressure:

$$P = -\frac{1}{Z} \sum_{i=1}^{\infty} e^{-\beta E_i} \left(\frac{\partial E_i}{\partial V} \right)_{\{n_i\}} \quad (8.488)$$

Partial differentiation of Z with respect to V gives:

$$\begin{aligned} \left(\frac{\partial Z}{\partial V} \right)_{T, \{n_i\}} &= \sum_{i=1}^{\infty} \left(\frac{\partial (e^{-\beta E_i})}{\partial V} \right)_{T, \{n_i\}} \\ &= \sum_{i=1}^{\infty} \frac{\partial (e^{-\beta E_i})}{\partial E_i} \times \frac{\partial E_i}{\partial V} = - \sum_{i=1}^{\infty} \beta e^{-\beta E_i} \left(\frac{\partial E_i}{\partial V} \right)_{T, \{n_i\}} \end{aligned} \quad (8.489)$$

Hence we can finally write P as:

$$P = \frac{1}{\beta Z} \left(\frac{\partial Z}{\partial V} \right)_{T, \{n_i\}} = \frac{1}{\beta} \left(\frac{\partial \ln(Z)}{\partial V} \right)_{T, \{n_i\}} \quad (8.490)$$

Evaluation of β :

First we differentiate Eq. (8.485) with respect to V :

$$\begin{aligned} \left(\frac{\partial U}{\partial V} \right)_T &= - \left[\frac{\partial}{\partial V} \left(\frac{\partial \ln(Z)}{\partial \beta} \right)_V \right]_T \\ &= - \left[\frac{\partial}{\partial \beta} \left(\frac{\partial \ln(Z)}{\partial V} \right)_T \right]_V \stackrel{(8.490)}{=} - \left[\frac{\partial}{\partial \beta} (\beta P) \right]_V \\ &= -P - \beta \left(\frac{\partial P}{\partial \beta} \right)_V \end{aligned} \quad (8.491)$$

Next we will recall Eq. (4.281):

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = -\frac{1}{T} \left[\frac{\partial P}{\partial (1/T)} \right]_V - P \quad (8.492)$$

where we have used the chain rule:

$$\partial P / \partial T = [\partial P / \partial (1/T)] [\partial (1/T) / \partial T] = - [\partial P / \partial (1/T)] / T^2$$

Now we can combine Eqs. (8.491) and (8.492):

$$-\beta \left(\frac{\partial P}{\partial \beta} \right)_V = -\frac{1}{T} \left(\frac{\partial P}{\partial (1/T)} \right)_V \quad (8.493)$$

Denote $Y \equiv \frac{1}{T}$. Then $\beta (\partial P / \partial \beta)_V = Y (\partial P / \partial Y)_V$ and hence:

$$\frac{\beta}{Y} = \left(\frac{\partial P}{\partial Y} \right)_V \left(\frac{\partial \beta}{\partial P} \right)_V = \left(\frac{\partial \beta}{\partial Y} \right)_V = \frac{d\beta}{dY} \quad (8.494)$$

In the last step we have noted that $\beta = \beta(T)$ only. The above differential equation can be integrated:

$$\begin{aligned} \frac{d\beta}{\beta} &= \frac{dY}{Y} \Rightarrow \ln(Y) = \ln(\beta) + C \\ &\Rightarrow \underbrace{\frac{1}{Y}}_{=1/T} = \underbrace{\frac{1}{C'}}_{=k} \times \beta \Rightarrow \beta = \frac{1}{kT} \end{aligned} \quad (8.495)$$

where k is the Boltzmann constant.

Now we can write complete expressions for Eqs. (8.485) and (8.490):

$$U = - \left(\frac{\partial \ln(Z)}{\partial \beta} \right)_{V, \{n_i\}} = - \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}} \frac{dT}{d\beta} \quad (8.496)$$

$$= - \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}} \left(-\frac{1}{k\beta^2} \right) = kT^2 \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}}$$

$$P = kT \left(\frac{\partial \ln(Z)}{\partial V} \right)_{T, \{n_i\}} \quad (8.497)$$

The complete form for Eq. (8.482) is:

$$p_i = \frac{e^{-E_i/(kT)}}{\sum_{j=1}^{\infty} e^{-E_j/(kT)}} = \frac{e^{-E_i/(kT)}}{Z} \quad (8.498)$$

Note that if the system contains degenerate (i.e., have the same energy) states, each of them must be included in Eq. (8.498) separately.

Evaluation of entropy S :

Consider a reversible process where only PV -work occurs. The 1st and 2nd laws of thermodynamics can be combined: $dU = TdS - PdV$. This gives:

$$dS = T^{-1}dU + PT^{-1}dV = d(T^{-1}U) + T^{-2}UdT + PT^{-1}dV \quad (8.499)$$

where we used $d(T^{-1}U) = -T^{-2}UdT + T^{-1}dU$. Substitution of Eqs. (8.496) and (8.497) for U and P gives:

$$dS = d(T^{-1}U) + k \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}} dT + k \left(\frac{\partial \ln(Z)}{\partial V} \right)_{T, \{n_i\}} dV \quad (8.500)$$

When $\{n_i\}$ are constant, the total differential is:

$$d \ln(Z) = \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}} dT + \left(\frac{\partial \ln(Z)}{\partial V} \right)_{T, \{n_i\}} dV \quad (8.501)$$

This allows us to rewrite Eq. (8.500) as:

$$dS = d(T^{-1}U) + kd(\ln(Z)) = d(T^{-1}U + k \ln(Z)) \quad (8.502)$$

Integration of this equation gives:

$$S = T^{-1}U + k \ln(Z) + C \quad (8.503)$$

It can be shown that $C = 0$ for most systems but we skip this lengthy consideration here. Thus:

$$S = \frac{U}{T} + k \ln(Z) = kT \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}} + k \ln(Z) \quad (8.504)$$

Note that other thermodynamic potentials such as G can be obtained by $G = U + PV - TS$.

8.2 Canonical partition function for a monoatomic ideal gas ³⁴⁷

Once system's partition function Z has been found, Eqs. (8.496), (8.497) and (8.498) can be used to calculate thermodynamic quantities. Exact calculation of Z for real systems is difficult because atoms/molecules interact and may require quantum mechanical calculations (i.e., to solve the Schrödinger equation). In the following, we will consider monoatomic ideal gas (distinguishable atoms), which means that we need to only consider translational motion of atoms (no vibration or rotation) and that the total energy can be expressed as a sum of individual atoms:

$$E_i = \sum_{j=1}^N \epsilon_{i,j} \quad (8.505)$$

where E_i is the total energy for state i , N the number of atoms and $\epsilon_{i,j}$ is the energy of atom j in state i . The canonical partition function Z can now be written as:

$$Z = \sum_{i=1}^{\infty} e^{-\beta E_i} = \sum_{i=1}^{\infty} e^{-\beta \sum_{j=1}^N \epsilon_{i,j}} \quad (8.506)$$

Since the atoms are distinguishable and i runs over all possible states, we can rewrite Eq. (8.506) as:

$$\begin{aligned} Z &= \overbrace{\sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \dots \sum_{m=1}^{\infty}}^{N \text{ times}} e^{-\beta(\epsilon_k + \epsilon_l + \dots + \epsilon_m)} \\ &= \sum_{k=1}^{\infty} e^{-\beta \epsilon_k} \times \sum_{l=1}^{\infty} e^{-\beta \epsilon_l} \times \dots \times \sum_{m=1}^{\infty} e^{-\beta \epsilon_m} \end{aligned} \quad (8.507)$$

Atomic partition functions are defined as:

$$z_j \equiv \sum_{i=1}^{\infty} e^{-\beta \epsilon_i} \text{ and } Z = z_1 \times z_2 \times \dots z_N \quad (8.508)$$

If the atoms are not all alike but there are N_A (do not confuse this with the Avogadro's number) atoms of species A, N_B atoms of species B, etc. then:

$$\begin{aligned} Z &= (Z_A)^{N_A} \times (Z_B)^{N_B} \times \dots \\ \text{where } Z_A &= \sum_{i=1}^{\infty} e^{-\beta \epsilon_{A,i,j}}, \dots \end{aligned} \quad (8.509)$$

Remember that this holds only for distinguishable particles (e.g., localized atoms in a solid).

349

It turns out that quantum mechanics excludes some classical states for indistinguishable particles and hence a different form of Eq. (8.509) must be used. It can be shown that at sufficiently high temperatures, the canonical partition function for indistinguishable particles is given by:

$$Z = \frac{z^N}{N!} \text{ and } z \equiv \sum_{i=1}^{\infty} e^{-\beta E_i} \quad (8.510)$$

where we have assumed that most molecules are in different microscopic states (see Physical Chemistry, Levine for more details). A mixture of species has then:

$$Z = \frac{(Z_A)^{N_A}}{N_A!} \times \frac{(Z_B)^{N_B}}{N_B!} \times \dots \quad (8.511)$$

The above formula cannot be used, for example, at liquid helium temperatures where the high temperature assumption does not hold.

8.3 Internal energy of monoatomic ideal gas

For monoatomic gas, we need to only consider translational motion (no rotation or vibration). In order to use Eq. (8.496), which here states that $U = kT^2 (\partial Z_{tr} / \partial T)_{V, \{n_i\}}$, we have to calculate the translational partition function Z_{tr} . If the atoms are treated as “particles in a box” (see quantum mechanics notes), Eq. (8.509) can be written as:

$$Z_{tr} = \frac{z_{tr}^N}{N!} = \frac{1}{N!} \left(\sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-(\beta h^2 / (8m)) \times (n_x^2 / a^2 + n_y^2 / b^2 + n_z^2 / c^2)} \right)^N \quad (8.512)$$

where h is the Planck’s constant (6.626076×10^{-34} J s), m is the atom mass, n_x , n_y and n_z are quantum numbers, and a, b, c define the volume where the atoms are confined (“the box”). When the quantized levels are close to each other, we can replace the above summations by integrals, for example:

$$\sum_{n_x=1}^{\infty} e^{-(\beta h^2 / (8m)) \frac{n_x^2}{a^2}} \approx \int_0^{\infty} e^{-(\beta h^2 / (8m)) \frac{n_x^2}{a^2}} dn_x = \frac{1}{2} \left(\frac{8m\pi}{\beta h^2} \right)^{1/2} a \quad (8.513)$$

Since $\beta = \frac{1}{kT}$ and $V = abc$, we can rewrite Eq. (8.512) as:

$$z_{tr} = (2\pi mkT/h^2)^{3/2} V \quad (8.514)$$

$$\ln(z_{tr}) = \frac{3}{2} \ln(2\pi mk/h^2) + \frac{3}{2} \ln(T) + \ln(V)$$

For N molecules we have:

$$\ln(Z_{tr}) = \ln\left(\frac{z_{tr}^N}{N!}\right) = N \ln(z_{tr}) - \ln(N!) \quad (8.515)$$

Now we can use Eq. (8.496) to evaluate U :

$$U = kT^2 \left(\frac{\partial \ln(Z)}{\partial T} \right)_{V, \{n_i\}} = \frac{3}{2} kNT^2 \times \frac{1}{T} = \frac{3}{2} kNT = \frac{3}{2} nRT \quad (8.516)$$

“Thermodynamics can tell us if a given process happens or not but it does not tell us how fast.”

This corresponds to Eq. (2.117) given earlier.

Examples of mixing processes:

- ◀ ◻ ▶ ◀ ▢ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡ 🔍 ↺

- ◀ ◻ ▶ ◀ ◻ ▶ ◀ ≡ ▶ ◀ ≡ ▶ ≡

9.2 The rates of chemical reactions

Rate of chemical reaction tells us how fast the given reaction occurs. The consumption of each reactant and product are dictated by this rate. The rate of chemical reaction r is always positive and is defined by:

$$r = \frac{1}{v_i} \frac{d[i](t)}{dt} \quad (9.517)$$

where v_i is the stoichiometric coefficient for i and $[i](t)$ denotes the concentration of i at a given time. Note that the stoichiometric coefficients are negative if i is on the left hand side of the chemical equation. The rate of consumption or production of i is denoted by r_i and directly given by its time derivative. Note, however, that this rate must also be positive and thus may require changing the sign of the derivative.

Example. Consider a reaction of the form $A + 2B \rightarrow 3C + D$. What is the rate of chemical reaction and what are the rates of the individual compounds?

Solution. The rate of chemical reaction is given by Eq. (9.517):

$$r = \frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt}$$

$$r_A = -\frac{d[A]}{dt}, r_B = -\frac{d[B]}{dt}, r_C = \frac{d[C]}{dt}, r_D = \frac{d[D]}{dt}$$

The SI unit for rate is $\text{mol L}^{-1} \text{s}^{-1}$.

Example. The rate of change in molar concentration of CH_3 radicals in the reaction $2\text{CH}_3(g) \rightarrow \text{CH}_3\text{CH}_3(g)$ is reported as $d[\text{CH}_3]/dt = -1.2 \text{ mol L}^{-1} \text{s}^{-1}$. What are the rate of reaction and the rate of formation of CH_3CH_3 ?

Solution. The rate of reaction is given by Eq. (9.517):

$$r = \frac{1}{-2} \frac{d[\text{CH}_3]}{dt} = \frac{1}{2} \times 1.2 \text{ mol L}^{-1} \text{s}^{-1} = 0.60 \text{ mol L}^{-1} \text{s}^{-1}$$

From stoichiometry of the reaction we can write:

$$r_{\text{CH}_3\text{CH}_3} = \frac{d[\text{CH}_3\text{CH}_3]}{dt} = -\frac{1}{2} \frac{d[\text{CH}_3]}{dt} = 0.60 \text{ mol L}^{-1} \text{s}^{-1}$$

It is often found that the rate of reaction is proportional to the concentrations of the reactants raised to a power. For example, for two reactants A and B , the rate law might be:

$$r = k[A][B] \quad (9.518)$$

where the proportionality constant k is called the *rate constant* for the reaction. Note that the rate constant is independent of the concentrations but may depend, for example, on temperature. For A and B reacting, Eq. (9.518) is called the *rate law* of the reaction. The general form of rate law is $r = f([A], [B], \dots)$ where f is a general function.

It should be emphasized that the rate law of a given reaction *can not usually be inferred from the chemical equation for the reaction*. Most chemical equations refer to a situation where multiple reactions occur to give the indicated outcome. Chemical equations where only one reaction occurs are called *elementary reactions*. It will turn out that the rate law and the chemical equation can only be directly related for elementary reactions. For this reason the rate law should always be obtained experimentally.

Example. Chemical reactions even with simple stoichiometry can result in very complicated rate law. For example, $\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr}(g)$ gives the following experimental rate law:

$$r = \frac{k [\text{H}_2] [\text{Br}_2]^{3/2}}{[\text{Br}_2] + k' [\text{HBr}]}$$

This is very different result that one would expect based on the chemical equation. Based on this we can conclude that this reaction is not elementary.

Once the rate law is known, we can use it to predict the rate of reaction at any point in time. As we will see later, it can also be used to predict the concentrations of each components at any point in time. The rate law can also give us important clues about the reaction mechanism itself as the two must be consistent. This would be especially useful for elementary reactions.

Many reactions are found to have rate laws of the form:

$$r = k [A]^a [B]^b \dots \quad (9.519)$$

where the powers (a and b) define the *order* of the reaction with respect to each species. The *overall order* of reaction is given by the sum of the individual orders, $a + b + \dots$. The reaction order does not have to be an integer and for many gas phase reactions they are not. Another special case is when the reaction order is zero (e.g., $a = 0$). This corresponds to *zeroth order reaction*, which means that the rate of reaction does not depend on the concentration of that particular component (e.g., $[A]^a = [A]^0 = 1$). The zeroth order behavior usually means that there is some other mechanism restricting the reaction rather than concentration. This could be, for example, catalyst surface area. Only heterogeneous reactions can have overall reaction order of zero. When the reaction is not of the form given by Eq. (9.519), the reaction orders are not defined and there the overall reaction order is not defined either. An example of this situation was given on the previous slide.

Example. Consider two reactions with the following rate laws: $r = k [A]^{1/2} [B]$ and $r = k [A]^0 = k$. What are the reactions orders with respect to A and B , and what are the overall reaction orders?

Solution. The first reaction has reaction order of $1/2$ with respect to A and 1 with respect to B . The overall reaction order is then $1/2 + 1 = 3/2$. For the second reaction the reaction order for A is zero and the overall reaction order is zero as well.

Determination of the rate law:

1. *Isolation method.* When the concentrations of all the reactants except one are in large excess, it is possible to determine the rate law with respect to this component. For example, considering reaction $A + B$ where B is in excess, the concentration of B stays approximately constant throughout the reaction. In this case, the rate law can be written:

$$r = k [A]^a [B]^b \approx k' [A]^a \quad (9.520)$$

where $k' = k [B]^b$ is approximately constant. By looking at the concentration of A as a function of time, it is now possible to determine a . When $a = 1$ above, the reaction is called *pseudofirst-order reaction*.

2. *Method of initial rates.* The rate is measured at the beginning of the reaction for several different initial concentrations of reactants. This is often used together with the isolation method as follows. Suppose that the rate law with A isolated is $r = k [A]^a$. The initial rate r_0 is then given by $r_0 = k [A]_0^a$. This can be written as:

$$\log(r_0) = \log(k) + a \log([A]_0) \quad (9.521)$$

This shows that a plot of $\log(r_0)$ against $\log([A]_0)$ should give a straight line with slope a .

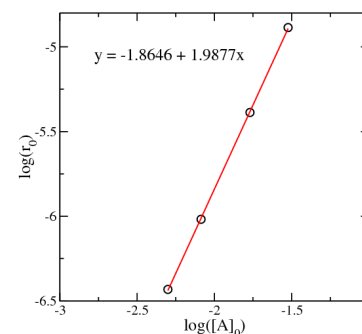
3. If the reaction order a is an integer, the reaction order can be often determined just by comparing the observed behavior with the integrated rate laws.

Example. The initial rate of reaction depends on concentration of a substance A as follows ($A \rightarrow P$):

$[A]_0$ (10^{-3} mol L $^{-1}$)	5.0	8.2	17	30
r_0 (10^{-7} mol L $^{-1}$ s $^{-1}$)	3.6	9.6	41	130

What is the order of reaction with respect to A and what is the rate constant?

Solution. Log-log plot of the data is shown below.



The slope is $1.99 \approx 2$ (2nd order) and $\log(k) = -1.8646 \Rightarrow k \approx 1.4 \times 10^{-2}$ (units?).

9.3 Integrated rate laws

By combining Eqs. (9.517) and (9.519), we can write for component i :

$$\frac{d[i]}{dt} = v_i k [A]^a [B]^b \dots \quad (9.522)$$

This is a differential equation for the unknown functions $[i](t)$. Most common solutions are considered below.

- *First-order reactions.* For a reaction $A \rightarrow$ products, we have $v_A = -1$ and for first-order reaction $a = 1$. Eq. (9.522) can now be written:

$$\frac{d[A]}{dt} = -k [A]^a = -k [A] \quad (9.523)$$

The solution to the above differential equation is an exponential function:

$$[A] = [A]_0 e^{-kt} \quad (9.524)$$

This is called the *integrated form* of the rate law. The unit for k in this equation is s^{-1} . The *half-life* $t_{1/2}$ (i.e., the time when half of the initial concentration is left) for a first-order reaction is given by:

$$\frac{[A]}{[A]_0} = \frac{1}{2} = e^{-kt_{1/2}} \Rightarrow t_{1/2} = \frac{\ln(2)}{k} \quad (9.525)$$

The numerical value for $\ln(2) \approx 0.693$.

- *Second-order reactions.* The second-order rate law is obtained from Eq. (9.522) when $a = 2$:

$$\frac{d[A]}{dt} = -k [A]^a = -k [A]^2 \quad (9.526)$$

The solution to this differential equation is (verify by differentiation):

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \text{ or } [A] = \frac{[A]_0}{1 + kt[A]_0} \quad (9.527)$$

The unit for the rate constant k in this case is $M^{-1} s^{-1}$ (or $L mol^{-1} s^{-1}$). The half-life in this case is given by:

$$t_{1/2} = \frac{1}{k [A]_0} \quad (9.528)$$

which can be derived the same way as we did for the 1st order reaction. Another type of second-order reaction is:

$$\frac{d[A]}{dt} = -k [A] [B] \quad (9.529)$$

where $a = b = 1$ and their sum gives two as is required for an over all second-order reaction. The solution to this differential equation is given by:

$$\ln \left(\frac{[B] / [B]_0}{[A] / [A]_0} \right) = ([B]_0 - [A]_0) kt \quad (9.530)$$

Note: When $[A] = [B]$, Eqs. (9.527) and (9.530) become identical as they describe the same rate law.

Example. Solve the differential equation given in Eq. (9.523).

Solution. We proceed first by rearranging the equation:

$$\frac{d[A]}{[A]} = -k dt$$

then we can integrate both sides:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

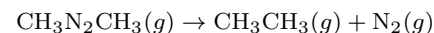
which gives after integration:

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt$$

This can be rearranged to correspond to Eq. (9.523):

$$[A] = [A]_0 e^{-kt}$$

Example. Consider the following reaction:



At 600 K the partial pressures of $\text{CH}_3\text{N}_2\text{CH}_3$ were found as follows:

t (s)	0	1000	2000	3000	4000
P (10^{-2} Torr)	8.20	5.72	3.99	2.78	1.94

Show that this reaction is 1st order in $\text{CH}_3\text{N}_2\text{CH}_3$ and find the rate constant at 600 K.

Solution. First we remember Eq. (1.11), which gives the relationship between the partial pressure of an ideal gas with its mole fraction:

$$P_i = \frac{n_i}{n} P = y_i P$$

where n_i is the number of moles of component i and n is the total number of moles present. Partial pressure P_i is proportional to the concentration of i :

$$P_i = \frac{n_i}{n} P = \frac{PV}{n} \times \frac{n_i}{V} = \underbrace{\frac{RT}{\text{constant}}}_{\text{constant}} \times \frac{n_i}{V} \propto \frac{n_i}{V} = c_i$$

where c_i is the concentration of species i and the gas mixture was assumed to follow the ideal gas law.

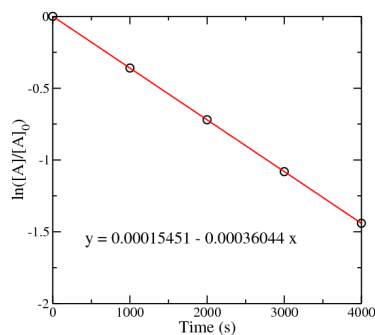
Note that in the 1st order integrated rate law the above proportionality constant drops out and therefore Eq. (9.524) can now be written:

$$P_i = P_{i,0}e^{-kt}$$

Here P_i is the partial pressure of $\text{CH}_3\text{N}_2\text{CH}_3$. Taking natural logarithms of this equation gives:

$$\ln\left(\frac{P_i}{P_{i,0}}\right) = -kt$$

Thus plotting $\ln(P_i/P_{i,0})$ as a function of t should give a straight line.



This plot is clearly linear indicating that the 1st order integrated rate law applies and the reaction is 1st order with respect to azomethane. The rate constant can be extracted directly from the slope as $k = -\text{slope} = 3.6 \times 10^{-4} \text{ s}^{-1}$.

Example. When gaseous ammonia decomposes on the surface of hot metal catalyst ($2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$), the half-life of $\text{NH}_3(g)$ was observed to depend on its initial pressure as follows:

P_0 (Torr)	65	105	150	185
$t_{1/2}$ (s)	290	460	670	820

What is the reaction rate and what is the value of rate constant?

Solution. First we observe that the half-life depends on the initial concentration and based on Eq. (9.525) this cannot be a first-order reaction. For a second-order reaction the half-life should depend inversely on the initial concentration (see Eq. (9.528)) but here we observe exactly the opposite trend and this cannot therefore be a second-order reaction either. If we write the rate law in the form (*zeroth-order reaction*):

$$\frac{d[A]}{dt} = -k[A]^0 = -k \quad (9.531)$$

The integrate rate law now becomes:

$$[A] - [A]_0 = -kt \quad (9.532)$$

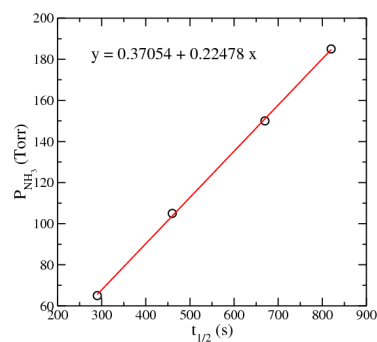
Inserting $[A] = [A]_0/2$ above, gives the half-life as:

$$t_{1/2} = \frac{[A]_0 - [A]_0/2}{k} = \frac{[A]_0}{2k} \quad (9.533)$$

Since this is a gas phase reaction, we replace the concentration by partial pressure (as we did in the previous example). Note that in this example the proportionality constant does not cancel out and we will get the rate constant in pressure units. We expect the half-life to depend on the initial pressure of $\text{NH}_3(g)$ as follows:

$$P_i = 2kt_{1/2}$$

Therefore a plot of the partial pressure as a function of $t_{1/2}$ should give a straight line with the slope $2k$.



The data yields a straight line and confirms that this reaction is zeroth-order. The rate constant (in pressure units) can be extracted from the slope: $k = \text{slope}/2 = 0.112 \text{ Torr s}^{-1}$. Note that linear regression analysis can also yield error estimates. Here the standard error estimate for the slope is ± 0.003 , which gives $0.0015 \text{ Torr s}^{-1}$ error for the rate constant. Thus we would report the final result as: $k = 0.112 \pm 0.002 \text{ Torr s}^{-1}$. Another important indicator is the correlation coefficient (r^2), which for this case was 0.9998 indicating a very good quality fit. Strong deviations from 1.0 would indicate a bad quality fit.

Example. Liquid phase reaction $\text{CH}_3\text{CH}_2\text{NO}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHNO}_2^-$ is second-order overall and the rate constant at 273 K is $k = 0.652 \text{ M}^{-1} \text{ s}^{-1}$. The initial concentration for nitroethane is 4.00 mM and 5.00 mM for OH^- . How long does the reaction have to proceed in order to consume 90% of the initial nitroethane concentration?

Solution. Let us denote nitroethane by A and OH^- by B . First we solve Eq. (9.530) for t :

$$t = \frac{1}{k([B]_0 - [A]_0)} \ln \left(\frac{[B]/[B]_0}{[A]/[A]_0} \right)$$

The current concentrations are $[A] = [A]_0 - x$ and $[B] = [B]_0 - x$ based on the stoichiometry of the chemical equation. 90% consumption of A (nitromethane) corresponds to 10% being left: $([A]_0 - x) / [A]_0 = 0.10$. Solving for x gives $x = 0.90 \times [A]_0 = 3.60 \text{ mM}$. Then $[A] = [A]_0 - x = 0.40 \text{ mM}$ and $[B] = [B]_0 - x = 1.40 \text{ mM}$. Inserting these values into the expression for t we get:

$$t = \frac{1}{0.652 \text{ M}^{-1} \text{ s}^{-1} (5.00 \times 10^{-3} \text{ M} - 4.00 \times 10^{-3} \text{ M})} \times \ln \left(\frac{1.40 \times 10^{-3} \text{ M} / 5.00 \times 10^{-3} \text{ M}}{0.40 \times 10^{-3} \text{ M} / 4.00 \times 10^{-3} \text{ M}} \right) = 1580 \text{ s}$$

Summary of the rate laws:

Order	Reaction	Rate law	$t_{1/2}$
0	$A \rightarrow P$	$r = k$ $[A] = [A]_0 - kt$	$\frac{[A]_0}{2k}$
1	$A \rightarrow P$	$r = k [A]$ $[A] = [A]_0 e^{-kt}$	$\frac{\ln(2)}{k}$
2	$A \rightarrow P$	$r = k [A]^2$ $[A] = \frac{[A]_0}{1 + kt[A]_0}$	$\frac{1}{k[A]_0}$
	$A + B \rightarrow P$	$r = k [A] [B]$ $\ln \left(\frac{[B]/[B]_0}{[A]/[A]_0} \right) = ([B]_0 - [A]_0) kt$	
3	$A + 2B \rightarrow P$	$r = [A] [B]^2$ $kt = \frac{\ln \left(\frac{[B][A]_0}{[A][B]_0} \right)}{([B]_0 - 2[A]_0)^2} + \frac{[B] - [B]_0}{([B]_0 - 2[A]_0)[B][B]_0}$	
$n \geq 2$	$A \rightarrow P$	$r = k [A]^n$ $kt = \frac{1}{n-1} \left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right)$	$\frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

9.4 Reactions approaching equilibrium

Previously we have assumed that the forward reaction is dominating and therefore we have ignored the possibility for the reaction to go from right to left. When the reaction approaches equilibrium, we have to consider both forward and backward reactions.

1. First-order reactions. Consider equilibrium $A \rightleftharpoons B$ where reactions $A \rightarrow B$ and $A \leftarrow B$ occur simultaneously at appreciable rate. The rate constant for the forward reaction is denoted by k_+ and backward reaction by k_- . Both reactions are taken to be first order. For example, A and B could correspond to two different isomers of a molecule. The forward rate $r_+ = k_+ [A]$ and backward rate $r_- = k_- [B]$. The rate law in terms of A can then be written as:

$$\frac{d[A]}{dt} = -k_+ [A] + k_- [B] \quad (9.534)$$

where the first term on the right hand side is responsible for the disappearance of A and the second term for producing more A . Given the initial concentration of A as $[A]_0$, the following balance has to hold at all times: $[A] + [B] = [A]_0$. Then we can write Eq. (9.534) as:

$$\frac{d[A]}{dt} = -k_+ [A] + k_- ([A]_0 - [A]) = -(k_+ + k_-) [A] + k_- [A]_0 \quad (9.535)$$

The solution to this differential equation is (verification by differentiation):

$$[A] = \frac{k_- + k_+ e^{-(k_+ + k_-)t}}{k_+ + k_-} [A]_0 \quad (9.536)$$

Equilibrium condition is reached after we wait long enough for the system to settle down (“steady-state”). Thus we take the limit of $t \rightarrow \infty$ above and obtain an expression for the equilibrium concentration of A :

$$[A]_{eq} = \frac{k_- [A]_0}{k_+ + k_-} \quad (9.537)$$

Since the concentrations of A and B are related to each other, we can get the equilibrium concentration of B :

$$[B]_{eq} = [A]_0 - [A]_{eq} = [A]_0 \left(1 - \frac{k_-}{k_+ + k_-} \right) = \frac{k_+ [A]_0}{k_+ + k_-} \quad (9.538)$$

If we approximate activities by concentrations, the equilibrium constant can be written for this reaction as (see Eq. (5.301)):

$$K = \frac{[B]_{eq}}{[A]_{eq}} \quad (9.539)$$

Inserting the equilibrium concentrations from Eq. (9.538) into Eq. (9.539), we get:

$$K = \frac{k_+}{k_-} \quad (9.540)$$

This is consistent with the statement saying that the forward and backward rates must be equal ($k_+ [A]_{eq} = k_- [B]_{eq}$) at equilibrium. If the equilibrium constant K and one of the rates are known then the remaining rate constant can be calculated. For a general reaction, the equilibrium constant can be expressed as:

$$K = \frac{k_{a,+}}{k_{a,-}} \times \frac{k_{b,+}}{k_{b,-}} \times \dots \quad (9.541)$$

We have now established an important link between the rates of reaction and thermodynamic equilibrium.

Example. 1,2-dimethylcyclopropane *cis* – *trans* isomerization follows first-order kinetics. At 726 K the *trans* isomer was observed to form according to:

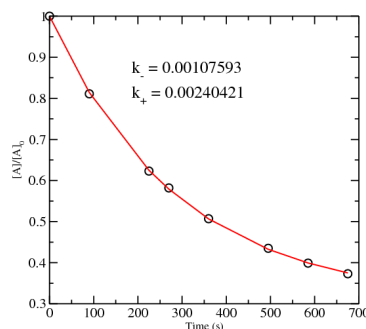
t (s)	0	90	225	270	360	495	585	675	∞
% <i>trans</i>	0	18.9	37.7	41.8	49.3	56.5	60.1	62.7	70.0

Calculate the equilibrium constant K and the rate constants k_+ (forward) and k_- (backward).

Solution. We can directly fit the data to Eq. (9.536). Since the two variables appear there separately, it is possible to determine them separately from this data. Once we get k_+ and k_- , we can use Eq. (9.540) to calculate K .

$$\frac{[A]}{[A]_0} = \frac{k_- + k_+ e^{-(k_+ + k_-)t}}{k_+ + k_-}$$

The data was not given in concentration units but percentages of B . Concentrations are proportional to % and the proportionality constant cancels out for first-order reactions. The concentration of A is proportional to $100\% - \%$ of *trans*. Fitting the given data to Eq. (9.536) is not a trivial matter. The equation is non-linear, which requires the non-linear least squares procedure. The result is shown below.



We identify $k_+ = 2.40 \times 10^{-3} \text{ s}^{-1}$ and $k_- = 1.08 \times 10^{-3} \text{ s}^{-1}$. This gives $K = 2.40 \times 10^{-3} / 1.08 \times 10^{-3} \text{ s}^{-1} = 2.22$. Non-linear least squares analysis is included in software packages like qtiplot, which is available from: <http://soft.proindependent.com/qtiplot.html>.

2. Relaxation kinetics. The term *relaxation* here denotes the return of a system to equilibrium after some given perturbation. This way we can study the relaxation kinetics near the equilibrium. An example of suitable perturbation could be a temperature jump that alters the equilibrium constant and hence the system will try reach the new equilibrium condition. It is possible to reach temperature jumps of 5-10 K in μs timescale. Other examples of perturbation are laser and microwave fields. Based on the van't Hoff equation (Eq. (5.323)), the equilibrium constant K depends on temperature provided that $\Delta_r H^\circ$ is non-zero, which we assume in the following.

Consider equilibrium $A \rightleftharpoons B$, which is a first-order reaction. If the temperature changes, the equilibrium constant $K = K(T)$ changed as well. Based on Eq. (9.541), the rate constants also depend on temperature $k_+ = k_+(T)$ and/or $k_- = k_-(T)$. The response of the system will be *exponential* as shown below.

Consider first the equilibrium condition:

$$\frac{d[A]_{eq}}{dt} = -k_+[A]_{eq} + k_-[B]_{eq} \quad (9.542)$$

Since we are at equilibrium $\frac{d[A]_{eq}}{dt} = 0$ and the forward and backward rates are equal: $k_+[A]_{eq} = k_-[B]_{eq}$. Next the system is perturbed in such a way that the reaction will try to reach new equilibrium concentrations given by $[A] = [A]_{eq} + \epsilon$ and $[B] = [B]_{eq} - \epsilon$. The former equation also defines the differential $d[A] = d\epsilon$. Now the system starts evolving according to:

$$\frac{d[A]}{dt} = -k_+ [A] + k_- [B] \quad (9.543)$$

where the rate constants k_+ and k_- now refer to the new values after perturbation. This equation can be written in terms of ϵ as:

$$\frac{d\epsilon}{dt} = -k_+ ([A]_{eq} + \epsilon) + k_- ([B]_{eq} - \epsilon) \quad (9.544)$$

Since the forward and backward rates are equal, this simplifies to:

$$\begin{aligned} \frac{d\epsilon}{dt} &= - \underbrace{(k_+ + k_-)}_{\equiv 1/\tau, \text{const.}, >0} \epsilon \\ \Rightarrow \epsilon &= \epsilon_0 e^{-t/\tau} \end{aligned} \quad (9.545)$$

where ϵ_0 is the change in concentration right after the temperature jump. From the exponential relaxation, we can obtain the sum of the new rate constants. When this is combined with the equilibrium condition, $K = \frac{k_+}{k_-}$, it is possible to obtain both rate constants individually.

9.5 The temperature dependence of reaction rates

The rate constants for most chemical reactions increase as temperature is increased. At low temperatures it is possible that some reactions, which are based on the quantum mechanical tunneling, have rates that do not depend on temperature. The relationship between rate constants, temperature, and the activation energies is often found to follow the *Arrhenius law* (Svante Arrhenius, Swedish chemist, 1859 – 1927):

$$k = Ae^{-E_a/(RT)} \quad (9.546)$$

where k is the rate constant, A is the *pre-exponential factor* or the *frequency factor*, E_a is the activation energy for the reaction, R is the gas constant, and T is the temperature. An alternative form for this equation is:

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad (9.547)$$

The parameter E_a can be obtained from the slope when plotting $\ln(k)$ as a function of $1/T$ and A from the intercept. These parameters are called *Arrhenius parameters*. Eq. (9.547) can be also written at two different temperatures as:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (9.548)$$

where the indices k_1 and k_2 refer to rate constants at T_1 and T_2 , respectively.

Derivation of the Arrhenius law. Consider reaction $A \rightarrow B$, which proceeds through a *transition state* denoted by A^* . Transition state is a molecular configuration along the reaction path where the energy has the maximum value. The reaction can then be written as:



The equilibrium constant for the first part of the reaction can be written as:

$$K = \frac{k_+}{k_-} = \frac{[A^*]}{[A]} \quad (9.550)$$

It is plausible to assume that $[A^*] \ll [A]$ since the intermediate A^* should be transient in nature. The concentration of the product B follows the first-order kinetics:

$$\frac{d[B]}{dt} = k[A^*] = \underbrace{kK}_{\equiv k'}[A] = k'[A] \quad (9.551)$$

where we used Eq. (9.550) in the last step and we introduced rate constant k' for the formation of B from A . Note that the rate constant k' applies for the whole reaction $A \rightarrow B$. Next we apply the van't Hoff equation (Eq. (5.323)):

$$\frac{\partial(\ln(K))}{\partial T} = \frac{\Delta_r H^{\circ*}}{RT^2} \approx \frac{E_a}{RT^2} \quad (9.552)$$

where K is the equilibrium constant between the initial and the transition states and $\Delta_r H^{\circ*}$ is the reaction enthalpy between these states. In the last step we have approximated $\Delta_r H^{\circ*} \approx E_a$. Since $K = k'/k$, Eq. (9.552) becomes:

$$\frac{\partial(\ln(k'))}{\partial T} - \frac{\partial(\ln(k))}{\partial T} = \frac{E_a}{RT^2} \quad (9.553)$$

Arrhenius assumed that the formation of the product B from the transition state is independent of temperature and hence the second term on the left is zero:

$$\frac{\partial(\ln(k'))}{\partial T} = \frac{E_a}{RT^2} \quad (9.554)$$

Solution to this differential equation is given by:

$$k' = Ae^{-E_a/(RT)} \quad (9.555)$$

where the frequency factor A arises from integration of Eq. (9.554).

Caution should be exercised when interpreting E_a and A . The assumptions made in the derivation may not be always valid causing the model to fail. E_a is the minimum kinetic energy that reactants must have in order to form products. Not all encounters of the reactants lead to the formation of products. The pre-exponential factor is often related to the frequency of such collisions with the exponential part giving the success rate.

Example. Rasemization of pinene is a first-order reaction. The following rate constants were determined in the gas phase: $k_{457.7\text{ K}} = 3.7 \times 10^{-7} \text{ s}^{-1}$ and $k_{510.1\text{ K}} = 5.1 \times 10^{-5} \text{ s}^{-1}$. Use the Arrhenius law to obtain E_a and calculate the rate constant $k_{480\text{ K}}$.

Solution. We use Eq. (9.548) at the two given temperatures:

$$\ln \left(\frac{5.1 \times 10^{-5} \text{ s}^{-1}}{3.7 \times 10^{-7} \text{ s}^{-1}} \right) = - \frac{E_a}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{510.1 \text{ K}} - \frac{1}{457.6 \text{ K}} \right)$$

Solving for E_a gives $E_a = 182 \text{ kJ mol}^{-1}$. The same equation can be used to obtain the rate constant at 480 K:

$$\ln \left(\frac{5.1 \times 10^{-5} \text{ s}^{-1}}{k_{480\text{ K}}} \right) = - \frac{182 \text{ kJ mol}^{-1}}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{510.1 \text{ K}} - \frac{1}{480 \text{ K}} \right)$$

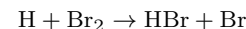
Solving for $k_{480\text{ K}}$ gives $3.5 \times 10^{-6} \text{ s}^{-1}$.

Note: When the Arrhenius equation fails, it is often observed that the following modified equation works well in practice (n is an empirical constant):

$$k = A' T^n e^{-E_a/(RT)}$$

9.6 Elementary reactions

Most chemical reactions occur in a sequence of steps called *elementary reactions*. An example of an elementary reaction is:



The *molecularity* of an elementary reaction is the number of molecules coming together to react in an elementary reaction. An elementary reaction is said to be *unimolecular reaction* if a single molecule reacts by itself (e.g., isomerization, decomposition). In a *bimolecular reaction*, a pair of molecules collide and exchange energy, atoms, or groups of atoms. Note: *reaction order and molecularity are not necessarily the same!* Reaction order is an empirical quantity whereas the molecularity is defined by the chemical equation of an elementary reaction.

Unimolecular elementary reaction. The rate law is first-order in the reactant:

$$A \rightarrow P \quad \frac{d[A]}{dt} = -k[A] \quad (9.556)$$

where P denotes products.

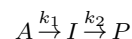
Bimolecular elementary reaction. The rate law is second order over all:

$$A + B \rightarrow P \quad \frac{d[A]}{dt} = -k[A][B] \quad (9.557)$$

Trimolecular elementary reaction. These reactions would follow third order kinetics. However, they are very rare as three molecules must to collide at the same time.

9.7 Consecutive elementary reactions

A *reaction mechanism* consists of a certain number of elementary steps. This can be a series of first and second order reactions, which occur sequentially or in parallel. The simplest consecutive elementary reaction can be written as:



Next we derive the expressions for $[A]$, $[I]$, and $[P]$. The rate of unimolecular decomposition of A into I is:

$$\frac{d[A]}{dt} = -k_1 [A] \quad (9.558)$$

The intermediate I formed from A according to:

$$\frac{d[I]}{dt} = k_1 [A] - k_2 [I] \quad (9.559)$$

and the product P :

$$\frac{d[P]}{dt} = k_2 [I] \quad (9.560)$$

Eq. (9.558) is just a first-order decay:

$$[A] = [A]_0 e^{-k_1 t} \quad (9.561)$$

381

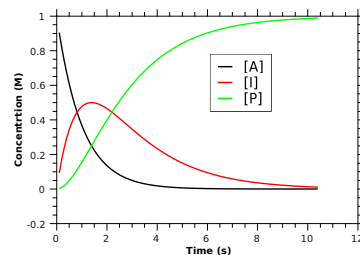
382

When the above result is substituted into Eq. (9.559) and we solve the resulting differential equation, we get ($[I]_0$):

$$[I] = \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) [A]_0 \quad (9.562)$$

Since we must have at all times $[A] + [I] + [P] = [A]_0$, we can solve for the concentration of P :

$$[P] = \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right) [A]_0 \quad (9.563)$$



The concentrations of A , I , and P are plotted on the left with $k_1 = 2k_2 = 1$ and $[A]_0 = 1$. A experiences an exponential decay, I starts building up and then decreases as it finally starts producing P .

If one of the consecutive steps is much slower than the other(s), it is said to be the *rate determining step*. For example, when $k_2 \gg k_1$ all I that is formed will rapidly convert into P . This can be seen by first noting that now: $e^{-k_2 t} \ll e^{-k_1 t}$ and $k_2 - k_1 \approx k_2$. Eq. (9.563) then reduces to:

$$[P] \approx (1 - e^{-k_1 t}) [A]_0 \quad (9.564)$$

This shows that the formation rate of P depends only on the smaller of the rate constants (k_1 above). In general the elementary reaction with the smallest rate constant in a given reaction scheme is the rate determining step.

Steady-state approximation. If we assume that the intermediate concentration is independent of time, we set its time derivative to zero:

$$\frac{d[I]}{dt} \approx 0 \quad (9.565)$$

This is called the *steady-state approximation*. If the original differential equation(s) are difficult to solve, one can use this approximation to simplify the calculation. When this is applied to $[I]$ in Eqs. (9.561), (9.562), and (9.563), we obtain:

$$[I] \approx \frac{k_1}{k_2} [A] \quad (9.566)$$

Substitution into Eq. (9.560) gives then:

$$\frac{d[P]}{dt} = k_2 [I] \approx k_1 [A] \quad (9.567)$$

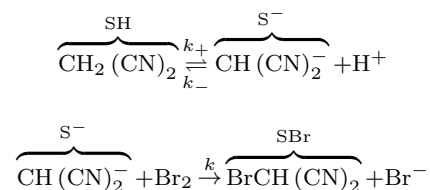
This shows that P in this case would be formed through the first-order decay of A with rate constant k_1 (corresponding to the rate determining step). Integration of this equation gives directly:

$$[P] = (1 - e^{-k_1 t}) [A]_0 \quad (9.568)$$

Example. Consider the following reaction:



The reaction mechanism has been determined as follows:



Write down the kinetic differential equations for SH, S⁻, and SBr. Apply the steady-state approximation for [S⁻] and use this result to eliminate [S⁻] from the kinetic expressions for SH and SBr.

Solution. The reactions that appear in the reaction mechanism must be elementary reactions. Therefore we can write the kinetic differential equations as:

$$\begin{aligned}\frac{d[\text{SH}]}{dt} &= -k_+ [\text{SH}] + k_- [\text{S}^-] [\text{H}^+] \\ \frac{d[\text{S}^-]}{dt} &= k_+ [\text{SH}] - k_- [\text{S}^-] [\text{H}^+] - k [\text{S}^-] [\text{Br}_2] \\ \frac{d[\text{SBr}]}{dt} &= k [\text{S}^-] [\text{Br}_2]\end{aligned}$$

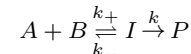
The steady-state approximation for S⁻ can be obtained by setting $d[\text{S}^-]/dt = 0$. The second equation above then gives:

$$[\text{S}^-] = \frac{k_+ [\text{SH}]}{k_- [\text{H}^+] + k [\text{Br}_2]}$$

This can be used to eliminate [S⁻] from the other kinetic equations:

$$-\frac{d[\text{SH}]}{dt} = \frac{d[\text{SBr}]}{dt} = \frac{k_+ k [\text{SH}] [\text{Br}_2]}{k_- [\text{H}^+] + k [\text{Br}_2]}$$

Pre-equilibrium conditions. If one of the consecutive steps involve both forward and backward reactions, we have to account for this in the kinetic differential equations. Consider the following reaction:



Note that it is possible to establish equilibrium in this reaction only if $k_- \gg k$. If this is the case then we can write an approximate equilibrium condition between $A + B$ and I as:

$$K = \frac{[I]}{[A][B]} \text{ with } K = \frac{k_+}{k_-} \quad (9.569)$$

The formation rate of P can now be written:

$$\frac{d[P]}{dt} = k[I] = kK[A][B] \quad (9.570)$$

Thus this is effectively a second-order rate law with an effective rate constant:

$$\frac{d[P]}{dt} = k'[A][B] \text{ with } k' = kK = \frac{k_+ k}{k_-} \quad (9.571)$$

Note: The above calculation can also be carried out without the assumption $k_- \gg k$ by using the steady-state approximation for the intermediate. In this case the effective rate constant can be obtained as:

$$k' = \frac{k_+ k}{k_- + k} \quad (9.572)$$

The corresponding steady-state concentration for I is given by

$$[I] \approx \frac{k_+ [A] [B]}{k_- + k} \quad (9.573)$$

This type of reactions are found, for example, in enzyme catalysis (the Michaelis-Menten mechanism).

Exercise. Derive Eqs. (9.572) and (9.573) by using the steady-state approximation for I .

Notes:

- ▶ There are many topics in chemical kinetics that are not covered by the above discussion. These include complex reactions such as chain reactions (including polymerization), explosions, photochemical reactions, catalytic reactions, and oscillating reactions.
- ▶ A given reaction mechanism may contain many reactions that are consecutive/parallel etc. and it often becomes impossible to find analytical solutions to the corresponding differential equations.
- ▶ A comprehensive kinetics database has been compiled by NIST and is available online at: <http://kinetics.nist.gov/kinetics/>.