Thermodynamics: Examples for chapter 2.

1. Metallic sodium reacts with water according to:

$$2\mathrm{Na} + 2\mathrm{H_2O} \rightarrow 2\mathrm{NaOH} + \mathrm{H_2}$$

If a mole of sodium metal is added to water, how much work is done on the atmosphere (i.e., open beaker; reversible process) by the subsequent reaction if the temperature is constant at 25 °C? Assume that H_2 is an ideal gas.

<u>Solution:</u>

$$\mathrm{Na}(s) + 2\mathrm{H_2O}(l) \rightarrow \mathrm{NaOH}(aq) + \frac{1}{2}\mathrm{H_2}(g)$$

One mole of Na produces half a mole of H_2. Using the ideal gas law:

$$V = \frac{nRT}{P} = \frac{0.5 \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K})}{(101325\ \mathrm{Pa})} \approx 0.0123\ \mathrm{m^3}$$

The PV-work is given then by:

$$w = -P\Delta V = -(101325\ \mathrm{Pa}) \times (0.0123\ \mathrm{m^3}) = -1.24\ \mathrm{kJ}$$

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2. Show that the differential df is inexact (a, b, c are constants).

$$df = \left(2ax^2 + bxy\right) dx + \left(bx^2 + 2cxy\right) dy$$

Does the corresponding line integral depend on the path? Furthermore, show that differential df/x is exact.

<u>Solution:</u>

Differential $df = Mdx + Ndy$ is exact if $\left(\frac{\partial N(x,y)}{\partial x}\right)_y = \left(\frac{\partial M(x,y)}{\partial y}\right)_x$. Here we have:

$$M = 2ax^2 + bxy \text{ and } N = bx^2 + 2cxy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = bx \text{ and } \left(\frac{\partial N}{\partial x}\right)_y = 2bx + 2cy$$

Because the partial derivatives are not equal, the differential is inexact. Line integrals for inexact differentials depend on path in general. For df/x we have:

$$M = 2ax + by \text{ and } N = bx + 2cy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = b \text{ and } \left(\frac{\partial N}{\partial x}\right)_y = b$$

Because the partial derivatives are equal, differential df/x is exact.

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3. Show that the following differential is inexact:

$$df = \left(y^2 - xy\right)dx - x^2dy$$

Test the integrating factor $\frac{1}{xy^2}$ to see if it produces an exact differential.

Solution:

$$M = y^2 - xy \text{ and } N = -x^2$$

$$\left(\frac{\partial M}{\partial y}\right)_x = 2y - x \text{ and } \left(\frac{\partial N}{\partial x}\right)_y = -2x$$

Because the partial derivatives are not equal, the differential is inexact. If we divide the differential by xy^2, we have:

$$M = \frac{1}{x} - \frac{1}{y} \text{ and } N = -\frac{x}{y^2}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{1}{y^2} \text{ and } \left(\frac{\partial N}{\partial x}\right)_y = -\frac{1}{y^2}$$

and hence differential $\frac{df}{xy^2}$ is inexact (difference in sign only!).

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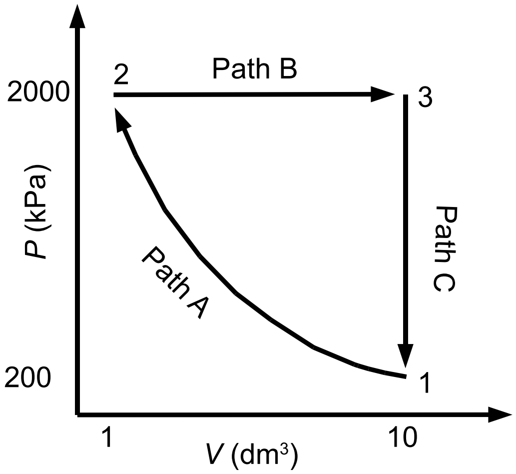
4. The state of monoatomic ideal gas ($n = 1$ mol) is changed reversibly as follows:

$$1 \xrightarrow{\text{A}} 2 \xrightarrow{\text{B}} 3 \xrightarrow{\text{C}} 1$$

where 1, 2, 3 and 4 refer to states and A, B and C to processes. Process A is isothermal, B is isobaric and C is isochoric. The cycle is described by the attached graph.



What are ΔU, ΔH, q and w after each process (A, B, C), temperatures at points 1, 2, 3, and w for the whole cycle? Note that for an ideal gas we have: $\bar{U} = \frac{3}{2}RT$ and $\bar{H} = \frac{5}{2}RT$.

Solution:

(a) Isothermal process A. Temperature after A, denoted by T_2, is given by the ideal gas law:

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(2000 \times 10^3 \text{ N m}^{-2})(10^{-3} \text{ m}^3)}{(1 \text{ mol})(8.314 \text{ N m mol}^{-1} \text{ K}^{-1})} = 240.6 \text{ K}$$

Both U and H depend only on temperature for ideal gases. This is an isothermal process and hence both ΔU and ΔH are zero. The PV-work in this step is given by (see lecture notes):

$$w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= -(1 \text{ mol}) \times \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right) \times (240.6 \text{ K}) \times \ln\left(\frac{1 \text{ dm}^3}{10 \text{ dm}^3}\right) = 4.6 \text{ kJ}$$

According to the first law of thermodynamics:

$$\Delta U = q + w \Rightarrow q = \Delta U - w = 0 - 4.6 \text{ kJ} = -4.6 \text{ kJ}$$

(b) Isobaric process B. The temperature at 3 is given by the ideal gas law:

$$T_3 = \frac{P_3 V_3}{nR} = \frac{(2000 \times 10^3 \text{ N m}^{-2})(10^{-2} \text{ m}^3)}{(1 \text{ mol})(8.314 \text{ N m mol}^{-1} \text{ K}^{-1})} = 2406 \text{ K}$$

Changes in the internal energy and enthalpy are given by:

$$\Delta U = \frac{3}{2} nR\Delta T = \frac{3}{2} nR (T_3 - T_2)$$

$$= 1.5 \times (1 \text{ mol}) \times \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right) \times (2406 \text{ K} - 240.6 \text{ K}) = 27.0 \text{ kJ}$$

$$\Delta H = \frac{5}{2} nR\Delta T = 45.0 \text{ kJ}$$

The first law states: $\Delta U = q + w$ and thus if we know either q or w, we can always calculate the other. In the isobaric case the work can be obtained with $P_{ext} = P$ and $dw = -PdV$. Integration of this equation gives: $w = -P\Delta V = -(2000 \times 10^3 \text{ Nm}^{-2}) \times (10 \times 10^{-3} \text{ m}^3 - 1.0 \times 10^{-3} \text{ m}^3) = -18.0$ kJ. And further $q = 27.0 \text{ kJ} - (-18.0 \text{ kJ}) = 45.0$ kJ.

(c) Isochoric process C. The temperature at point 1 is given by the ideal gas law:

$$T_1 = \frac{P_1 V_1}{nR} = 240.6 \text{ K}$$

Changes in the internal energy and enthalpy are given by:

$$\Delta U = \frac{3}{2} nR\Delta T = 1.5 \times (1 \text{ mol}) \times \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right) \times (240.6 \text{ K} - 2406 \text{ K}) = -27.0 \text{ kJ}$$

$$\Delta H = \frac{5}{2} nR\Delta T = 2.5 \times (1 \text{ mol}) \times \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right) \times (240.6 \text{ K} - 2406 \text{ K}) = -45.0 \text{ kJ}$$

The volume is constant and hence $w = 0$ kJ. The first law gives $q = -27.0$ kJ. The total work in the cycle is: $w_{tot} = w_\mathrm{A} + w_\mathrm{B} + w_\mathrm{C} = (4.61 - 18.0 + 0.00)$ kJ $= -13.4$ kJ.

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5. One mole of nitrogen (ideal gas) at 25 °C and 1 bar is expanded reversibly and isothermally to a pressure of 0.132 bar. (a) What is the value of w? (b) What is the value of w if the nitrogen is expanded against a constant external pressure of 0.132 bar?

Solution:

a) Based on the lecture notes, we have:

$$w = RT \ln\left(\frac{P_2}{P_1}\right) = \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times (298.15 \text{ K}) \times \ln\left(\frac{0.132 \text{ bar}}{1 \text{ bar}}\right) = -5.03 \text{ kJ mol}^{-1}$$

b) In (a) the pressure changes during the process. Here the external pressure is constant and we can directly calculate:

$$w = -P_{ext}\Delta V = -P_{ext}\left(V_2 - V_1\right)$$
$$V_1 = \frac{nRT}{P_1} = 0.0248 \text{ m}^3 \text{ and } V_2 = 0.188 \text{ m}^3$$

$$\Rightarrow w = -\left(0.132 \times 10^5 \text{ N m}^{-2}\right)\left(0.188 \text{ m}^3 - 0.0248 \text{ m}^3\right) = -2.15 \text{ kJ mol}^{-1}$$

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6. (a) Derive the equation for the work of reversible isothermal expansion of a van der Waals gas from V_1 to V_2.
   (b) A mole of CH_4 expands reversibly from 1 to 50 L at 25 °C. Calculate the work (in joules) assuming that the gas is ideal.
   (c) A mole of CH_4 expands reversibly from 1 to 50 L at 25 °C. Calculate the work (in joules) assuming that the gas obeys the van der Waals equation. For $CH_4(g)$, $a = 2.283$ L^2 bar mol^{-2} and $b = 0.04278$ L mol^{-1}.

Solution:

(a) PV-work of a van der Waals gas is given by:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$
$$w = -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{nRT}{V - nb} dV + \int_{V_1}^{V_2} \frac{an^2}{V^2} dV$$
$$= -nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) + an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

(b) The correspondig ideal gas result gives:

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -\left(1 \text{ mol}\right)\left(8.314 \text{ J K}^{-1}\text{mol}^{-1}\right)\left(298 \text{ K}\right) \ln\left(\frac{50 \text{ L}}{1 \text{ L}}\right)$$
$$= -9697 \text{ J}$$

(c) Using the result in (a) we get:

$$w = -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln\left(\frac{(50 \text{ L}) - (1 \text{ mol})(0.04278 \text{ L mol}^{-1})}{(1 \text{ L}) - (1 \text{ mol})(0.04278 \text{ L mol}^{-1})}\right)$$

$$+\left[\left(2.283 \text{ L}^2 \text{ bar mol}^{-2}\right) \times \left(10^{-6}\frac{\text{m}^6}{\text{L}^2}\right) \times \left(10^5\frac{\text{Pa}}{\text{bar}}\right)\right] \times$$

$$(1 \text{ mol})^2 \left(\frac{1}{(1 \text{ L}) \times (10^{-3}\text{L/m}^3)} - \frac{1}{(50 \text{ L}) \times (10^{-3}\text{L/m}^3)}\right)$$

$$= -9799 \text{ J} + 224 \text{ J} = -9575 \text{ J}$$

This is the work done by the gas (negative). The amount of work done on the surroundings is therefore 9575 J. Less work is done by methane than an ideal gas because of intermolecular interactions.

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7. Liquid water is vaporized at 10 °C and 1.013 bar in an open container (reversible process). The heat of vaporization is 40.69 kJ mol^{-1}. Assume that water vapor behaves like an ideal gas. What are the values of (a) w_{rev} per mole? (b) q per mole? (c) $\Delta\bar{U}$? (d) $\Delta\bar{H}$?

   Solution:

   (a) Assuming that water vapor is an ideal gas and that the volume of liquid water is negligible, we have (for one mole):

   $$w_{rev} = -P\Delta V = -P\frac{nRT}{P} = -nRT$$
   $$= -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(283.15 \text{ K}) = -2.35 \text{ kJ}$$

   (b) The heat of vaporization is 40.69 kJ mol^{-1}, which is the heat absorbed q and has a positive sign. Thus $q = 40.69$ kJ mol^{-1}.

   (c) The first law of thermodynamics gives:

   $$\Delta\bar{U} = q+w = (40.69 \text{ kJ mol}^{-1})+(-2.35 \text{ kJ mol}^{-1}) = 38.3 \text{ kJ mol}^{-1}$$

(d) By using the values from (a) and (c), we can now calculate $\Delta\bar{H}$:

$$\Delta\bar{H} = \Delta\bar{U} + \Delta(PV) = \Delta\bar{U} + P\Delta V = \Delta\bar{U} - w_{rev} = 40.7 \text{ kJ mol}^{-1}$$

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8. The heat capacities of a gas may be represented by the Shomate equation (see the NIST Chemistry Webbook):

$$\bar{C}_P = \alpha + \beta T + \gamma T^2 + \delta T^3 + \frac{\eta}{T^2}$$

For N_2 gas (between 298 K and 6000 K), $\alpha = 26.09200$ J K^{-1} mol^{-1}, $\beta = 8.218801 \times 10^{-3}$ J K^{-2} mol^{-1}, $\gamma = -1.976141 \times 10^{-6}$ J K^{-3} mol^{-1}, $\delta = 0.159274 \times 10^{-9}$ J K^{-4} mol^{-1} and $\eta = 0.044434 \times 10^{6}$ J K mol^{-1}. How much heat is required to heat one mole of N_2 from 300 K to 1000 K?

Solution:

$$q = \int_{T_1}^{T_2} \bar{C}_P dT = \alpha T_2 + \frac{\beta}{2}T_2^2 + \frac{\gamma}{3}T_2^3 + \frac{\delta}{4}T_2^4 - \frac{\eta}{T_2} - \alpha T_1 - \frac{\beta}{2}T_1^2 - \frac{\gamma}{3}T_1^3 - \frac{\delta}{4}T_1^4 + \frac{\eta}{T_1}$$

When the constants are inserted in the above expression, we get $q = 21.506$ kJ mol^{-1}.

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9. A mole of argon (ideal gas) is allowed to expand adiabatically and reversibly from a pressure of 10 bar and 298.15 K to 1 bar. What is the final temperature and how much work is done on the argon gas?

Solution:

Recall the following equations from the lecture notes:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} \quad \text{where } \gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

For an ideal gas we have:

$$\bar{C}_V = \frac{3}{2}R \text{ and } \bar{C}_P = \frac{5}{2}R \Rightarrow \gamma = 5/3$$

Now we can solve for T_2:

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} = (298.15\text{ K})\left(\frac{1\text{ bar}}{10\text{ bar}}\right)^{2/5} = 118.70\text{ K}$$

The process is adiabatic which means that $q = 0$. The first law then gives $\Delta U = w$. Since $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gases, we have:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT$$

$$\Rightarrow w = \Delta U = \int\limits_{T_1}^{T_2} C_V dT = \frac{3}{2}R\left(T_2 - T_1\right)$$

$$= \frac{3}{2} \times \left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right) \times (118.70\text{ K} - 298.15\text{ K}) = -2238\text{ J mol}^{-1}$$

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10. Calculate $\Delta_r H^\circ$ at 298 K for:

$$\mathrm{H_2}(g) + \mathrm{F_2}(g) \rightarrow 2\mathrm{HF}(g)$$
$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\mathrm{HCl}(g)$$
$$\mathrm{H_2}(g) + \mathrm{Br_2}(g) \rightarrow 2\mathrm{HBr}(g)$$
$$\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightarrow 2\mathrm{HI}(g)$$

Use the data available in the NIST Chemistry Webbook (http://webbook.nist.gov/chemistry/).

Solution:

We use the following equation (see lecture notes):

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

By looking up the data from the table and using this equation, we get:

$$2\times(-273.30 \text{ kJ mol}^{-1})-(0 \text{ kJ mol}^{-1})-(0 \text{ kJ mol}^{-1}) = -546.6 \text{ kJ mol}^{-1}$$

$$2\times(-92.31 \text{ kJ mol}^{-1})-(0 \text{ kJ mol}^{-1})-(0 \text{ kJ mol}^{-1}) = -184.62 \text{ kJ mol}^{-1}$$

$$2\times(-36.29 \text{ kJ mol}^{-1})-(30.91 \text{ kJ mol}^{-1})-(0 \text{ kJ mol}^{-1}) = -103.49 \text{ kJ mol}^{-1}$$

$$2\times(26.50 \text{ kJ mol}^{-1})-(62.42 \text{ kJ mol}^{-1})-(0 \text{ kJ mol}^{-1}) = -9.42 \text{ kJ mol}^{-1}$$

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11. One gram of liquid benzene is burned in an adiabatic bomb calorimeter. The temperature before ignition was 20.826 °C, and the temperature after the combustion was 25.000 °C. The heat capacity of the bomb, the water around it, and the contents of the bomb before the combustion was 10 000 J K^{-1}. Calculate $\Delta_f H^\circ$ for $C_6H_6(l)$ at 298.15 K from these data. Assume that the water produced in the combustion is in the liquid state, the carbon dioxide produced in the combustion is in the gas state and all gases behave according to the ideal gas law. The combustion reaction is:

$$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$$

Solution:

Even though this is called adiabatic, there is heat exchange between the sample (liquid benzene; system) and the surrounding water bath around it. The adiabaticity means that there is no thermal contact between the bath and the rest of the world. The total volume of the system is constant, which means that $w = P\Delta V = 0$ and $\Delta U = q$. Thus the heat released to the bath must correspond to the change in internal energy of the system. The heat capacity of the system+bath was given, so we can relate the temperature increase in the bath to the amount of heat released from the system:

$$\Delta U = q = -\int_{T_1}^{T_2} C_{\text{system+bath}} dT = -C_{\text{system+bath}} \Delta T$$

$$= -\left(10 \text{ kJ K}^{-1}\right) \times (4.174 \text{ K}) = -41.74 \text{ kJ}^{-1}$$

where the minus signifies that heat flows out of the system). Since the molecular weight of benzene is 78 g mol^{-1} and we had 1 gram of benzene, we finally get: $\Delta U = -3255.7$ kJ mol^{-1}.

In order to get ΔH for the reaction, one must consider the fact that gaseous products are consumed/formed. Let's first write the equation in standard form:

$$C_6H_6(l) + 7.5O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$

So we see that when one mole of benzene burns, 7.5 moles of O_2 gas is consumed and 6 moles of CO_2 is formed. This means that the pressure in the bomb is not constant. Recall that $H = U + PV$ and hence $\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P$. The volume is constant, so we don't need to consider the $P\Delta V$ term. If we consider that both O_2 and CO_2 are ideal gases (the total amount of gas is denoted by n_{gas}), then we can write $\Delta(PV) = R\Delta(n_{gas}T) = RT\Delta n_{gas} + Rn_{gas}\Delta T \approx RT\Delta n_{gas}$. In this example, $\Delta n = 6.0 - 7.5 = -1.5$. Thus we have ($T = 298$ K):

$$\Delta \bar{H}_{298 \text{ K}} = \Delta \bar{U} + \frac{RT\Delta n_{gas}}{1 \text{ mol}} = -3255.7 \text{ kJ mol}^{-1} - 1.5RT/\text{mol} = -3259.4 \text{ kJ mol}^{-1}$$

From the NIST Chemistry Webbook we have the following values: $\Delta H_f(CO_2(g)) = -393.51$ kJ mol^{-1}, $\Delta H_f(H_2O(l)) = -285.83$ kJ mol^{-1} and $\Delta H_f(O_2(g)) = 0$ kJ mol^{-1}. If we write the reaction using heats of formation, we have:

$$\Delta H_f(C_6H_6(l)) + 7.5 \times \Delta H_f(O_2(g)) + \Delta H_{298 \text{ K}} = 6 \times \Delta H_f(CO_2(g)) + 3 \times \Delta H_f(H_2O(l))$$

Note that the '$-$' sign in $\Delta H_{298 \text{ K}}$ signifies that the system (benzene) is loosing energy and hence when we place it in the above equation

$\Delta H_{298\text{ K}}$ has a positive sign when it is put on the left hand side and negative when put on the right hand side. On the right hand side it would yield positive number, which states that energy is being released. By solving for $\Delta H_f(\mathrm{C_6H_6}(l))$ from this equation we get:

$$\Delta H_f(\mathrm{C_6H_6}(l)) = 6 \times (-393.51\text{ kJ mol}^{-1}) + 3 \times (-285.83\text{ kJ mol}^{-1})$$

$$-(-3259.4\text{ kJ mol}^{-1}) = 40.9\text{ kJ mol}^{-1}$$

(The literature value is *ca.* 49 kJ mol^{-1} – not a great measurement accuracy...)