Thermodynamics: Examples for chapter 3.

1. Show that $(\partial C_V/\partial V) = 0$ for a) an ideal gas, b) a van der Waals gas and c) a gas following $P = \frac{nRT}{V-nb}$. Assume that the following result holds:

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

Hint: In b) and c), differentiate with respect to both temperature and volume and recall that for exact differentials the order of differentiation can be exchanged.

<u>Solution:</u>

The lecture notes give: $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. Differentiate this equation with respect to volume:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$$

By using the relation given in the problem, we can write this as:

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

Next we consider the various equations of state:

a) Ideal gas. $P = nRT/V$ from which the second derivative of pressure (see above) is zero and therefore $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$.

b) For a van der Waals gas we have: $P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$. Differentiation of P with respect to T once just gives $nR/(V - nb)$. This does not depend on T and hence $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$.

c) Differentiation of P twice with respect to T again gives zero and hence $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$.

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2. Show that q_{rev} is not a state function (i.e. dq_{rev} is not exact) for a gas obeying the equation of state $P = \frac{RT}{V-b}$, but that d_{qrev}/T is. Assume a reversible process and consider only PV-work. Hint: you may proceed as follows:

   (a) Use the previous problem to calculate $(\partial U/\partial V)_T$.

   (b) Use $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ to calculate dU.

   (c) Use the first law of thermodynamics to get an expression for dq.

   (d) Substitute the equation of state into the above expression.

   (e) Apply the exactness test for differentials ($dq = M(V,T)dT + N(V,T)dV$). Use results from the previous problem to differentiate M with respect to V.

   (f) Repeat the same calculation for dq/T.

   <u>Solution:</u>

   By using the result given in the first problem, we can obtain $\left(\frac{\partial U}{\partial V}\right)_T = 0$. The total differential for dU now gives $dU = \left(\frac{\partial U}{\partial T}\right)_V dT$ and hence $dU = C_V dT$. The first law of thermodynamics, $dU = dq + dw$, gives $dq = C_V dT - dw$. Considering PV-work, we can write: $dq = C_V dT + P_{ext} dV$. Because the process is reversible, $P_{ext} = P$ and $dq = C_V dT + PdV$. For dq to be exact we should have:

   $$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

   From the first problem we know that the left hand side is zero. The right hand side, however, is not zero:
   $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \neq 0$
   Thus dq is inexact. For dq/T we have: $\frac{dq}{T} = \frac{C_V}{T} dT + \frac{P}{T} dV$. Now the exactness test gives:

   $$\left(\frac{\partial C_V/T}{\partial V}\right)_T = 0 \text{ (T is constant)}$$

$$\left(\frac{\partial(nR/(V-nb))}{\partial T}\right)_V = 0 \text{ (the expression does not depend on } T\text{)}$$

Thus dq/T is exact.

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3. An ideal gas initially at (P_1, V_1, T_1) undergoes a reversible isothermal expansion to (P_2, V_2, T_1) (path 1). The same change in state of the gas can be achieved by allowing it to expand adiabatically from (P_1, V_1, T_1) to (P_3, V_2, T_2) and then heating it at constant volume to (P_2, V_2, T_1) (path 2). Note that T_2 has not been specified and you should find an equation that determines it. Show that the entropy change for the reversible isothermal expansion (path 1) is the same as the sum of the entropy changes in the reversible adiabatic expansion and the reversible heating (path 2). Because the two paths give the same result, it is probable that the integral is independent of path. This is not a complete proof – why?

   Solution:

   Path 1: First we recall that for an ideal gas $U = \frac{3}{2}nRT$ (see lecture notes). The temperature is constant along this path and thus change in internal energy must be zero. The first law of thermodynamics now states that $\Delta U = q_{rev} + w_{rev}$ and hence $q_{rev} = -w_{rev}$. Recall the following equation from the lecture notes:

$$w_{rev} = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) \Rightarrow q_{rev} = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

   Using the definition of entropy gives:

$$\Delta S = \frac{q_{rev}}{T_1} = nR\ln\left(\frac{V_2}{V_1}\right)$$

   Path 2: First consider the first segment from (P_1, V_1, T_1) to (P_3, V_2, T_2). The expansion is adiabatic (i.e. no heat exchange with the surroundings) and hence $q_{rev} = 0$. For this reason the change in entropy is also zero ($\Delta S = q_{rev}/T = 0$). The final temperature in an adiabatic expansion is determined by integrating $C_V\frac{dT}{T} = -nR\frac{dV}{V}$ (see lecture notes):

$$\int_{T_1}^{T_2} \frac{C_V}{T} dT = -nR \int_{V_1}^{V_2} \frac{dV}{V} = -nR \ln\left(\frac{V_2}{V_1}\right)$$

Along the second segment (P_3, V_2, T_2) to (P_2, V_2, T_1), we have a constant volume process. The lecture notes now give $dq_{rev} = C_V dT$. The definition of entropy is $dS = \frac{dq_{rev}}{T}$ and thus:

$$dS = \frac{C_V dT}{T} \Rightarrow \Delta S = \int_{T_2}^{T_1} \frac{C_V dT}{T} = -\int_{T_1}^{T_2} \frac{C_V dT}{T}$$

Comparison of this with the expression determining T_2 along the first segment, gives the final result:

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

This is the same result that was obtained along path 1. For a complete proof of exactness, one would have to use the exactness test or consider infinitely many paths (or rather, the exactness test).

4. Water is vaporized reversibly at 100 °C and 1.01325 bar. The heat of vaporization is 40.69 kJ mol^{-1}. a) What is the value of ΔS for the water? b) What is the value of ΔS for the water plus the heat reservoir at 100 °C? The heat reservoir is thermally isolated from its surroundings.

   Solution:

   a) $\Delta S_{\mathrm{H_2O}} = \frac{q}{T} = \frac{40.69 \text{ kJ mol}^{-1}}{373.13\text{K}} = 109.04 \text{ J K}^{-1} \text{ mol}^{-1}$. Note that + sign means that water receives heat.

   b) The reservoir loses heat to water exactly the same amount as above. The change in entropy for the heat reservoir is $-q/T = -109.04 \text{ J K}^{-1} \text{ mol}^{-1}$.

Note: Since water + heat reservoir is isolated from the rest of the world, the total change its entropy is 0. The total entropy in the system is conserved.

5. Assuming that CO_2 is an ideal gas, calculate ΔH° and ΔS° for the following process:

$$\mathrm{CO_2}(g, 298.15\text{ K}, 1\text{ bar}) \rightarrow \mathrm{CO_2}(g, 1000\text{ K}, 1\text{ bar})$$

Consider 1 mol of gas and a reversible process. Given: $\bar{C}_P^\circ(T) = 26.648 + 42.262 \times 10^{-3}T - 142.4 \times 10^{-7}T^2$ (units: J K^{-1} mol^{-1}).

Solution:

Here ° refers to the standard state. For gases this is 1 bar pressure but note that this does not specify temperature. The overbar denotes that these are molar quantities (i.e. per mole). To calculate change in enthalpy, we integrate the heat capacity over temperature (see lecture notes):

$$\Delta\bar{H}^\circ = \int_{T_1}^{T_2} \bar{C}_P^\circ dT = \Big/_{298.15\text{ K}}^{1000\text{ K}} \left[26.648 \times T + \left(\frac{42.262 \times 10^{-3}}{2}\right)T^2 + \left(\frac{-142.40 \times 10^{-7}}{3}\right)T^3\right]$$

$$= 33.34\text{ kJ mol}^{-1}$$

Furthermore, at constant pressure we can apply equations: $dq = C_P dT$ and $dS = dq_{rev}/T = C_P/TdT$:

$$\Delta\bar{S}^\circ = \int_{T_1}^{T_2} \frac{\bar{C}_P^\circ}{T} dT = \Big/_{298.15\text{ K}}^{1000\text{ K}} \left[26.648 \times \ln(T) + 42.262 \times 10^{-3}T - \left(\frac{142.4 \times 10^{-7}}{2}\right)T^2\right]$$

$$= 55.42\text{ J K}^{-1}\text{ mol}^{-1}$$

6. Ammonia (considered to be an ideal gas) initially at 25 °C and 1 bar pressure is heated at constant pressure until the volume has trebled. Assume reversible process. Calculate: a) q per mole, b) w per mole, c) $\Delta\bar{H}$, d) $\Delta\bar{U}$, e) $\Delta\bar{S}$ given $\bar{C}_P = 25.895 + 32.999\times10^{-3}T - 30.46\times10^{-7}T^2$ (in J K^{-1} mol^{-1}).

   Solution:

   Tripling of the ideal gas volume ($PV_1 = nRT_1$) leads to $T = P(3V_1)/(nR)$, which means that the temperature will be three times higher; $T_2 = 3T_1$. Note that pressure is constant.

   a) $q = \int\limits_{T_1}^{T_2} \bar{C}_P dT = \int\limits_{298\text{ K}}^{894\text{ K}} (25.895 + 32.999\times10^{-3}T - 30.46\times10^{-7}T^2)\,dT =$ 26.4 kJ mol^{-1}.

   b) $w = -P\Delta\bar{V} = -R\Delta T = -\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)\times(596\text{ K}) =$ -4.96 kJ mol^{-1}.

   c) Because pressure is constant, we have $\Delta\bar{H} = q_P = 26.4$ kJ mol^{-1}.

   d) $\Delta\bar{U} = q + w = (26.4 - 4.96)$ kJ $\mathrm{mol}^{-1} = 21.4$ kJ mol^{-1}.

   e) $\Delta\bar{S} = \int\limits_{T_1}^{T_2} \frac{\bar{C}_P}{T} dT = \int\limits_{298\text{ K}}^{894\text{ K}} \left(\frac{25.895}{T} + 32.999\times10^{-3} - 30.46\times10^{-7}T\right)dT =$ 46.99 J K^{-1} mol^{-1}.

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7. Three moles of an ideal gas expand isothermally and reversibly from 90 L to 300 L at 300 K. a) calculate ΔU, ΔS, w and q for this system, b) calculate $\Delta\bar{U}$, $\Delta\bar{S}$, w per mole and q per mole, c) If the expansion is carried out irreversibly by allowing the gas to expand into and evacuated container, what are the values of $\Delta\bar{U}$, $\Delta\bar{S}$, w per mole and q per mole?

   Solution:

   a) Change in internal energy is zero because the gas is ideal. Recall that the internal energy for an ideal gas depends only on temperature. Here we have an isothermal process and hence no change in internal energy occurs, $\Delta U = 0$. Note also that the 1st law now states that $q = -w$. For an isothermal process (see the lecture notes) we have:

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

$$= (3 \text{ mol}) \times \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times (300 \text{ K}) \ln\left(\frac{300 \text{ L}}{90 \text{ L}}\right) = -9.01 \text{ kJ}$$

and $q = 9.01$ kJ. By using the definition of entropy, we can calculate the change in entropy:

$$\Delta S = \frac{q_{rev}}{T} = \frac{-9.01 \text{ kJ}}{300 \text{ K}} = 30.03 \text{ J K}^{-1}$$

b) Divide everything by 3 mol to get per mole quantities:

$$\Delta\bar{U} = 0 \text{ kJ mol}^{-1}, \Delta\bar{S} = 10.01 \text{ J K}^{-1} \text{ mol}^{-1},$$
$$w = -3.00 \text{ kJ mol}^{-1}, q = 3.00 \text{ kJ mol}^{-1}$$

c) Since the temperature is constant, we have $\Delta\bar{U} = 0$. Since the gas is expanding into vacuum, $P_{ext} = 0$ and thus $w = 0$. By the first law, $q = 0$. The entropy is the same as in b) because its value depends only on endpoints of the path. Note that q along the present irreversible path cannot be used in calculating entropy – one must always use a reversible path (for example that in b) above). For this reason $\Delta\bar{S} = 10.01 \text{ J K}^{-1} \text{ mol}^{-1}$, which is the same value as in b).

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8. An ideal gas at 298 K expands isothermally from a pressure of 10 bar to 1 bar. What are the values of w per mole, q per mole, $\Delta\bar{U}$, $\Delta\bar{S}$ in the following cases? a) The expansion is reversible, b) The expansion is free (irreversible), (c) The gas and its surroundings form an isolated system, and the expansion is reversible and d) The gas and its surroundings form an isolated system, and the expansion is free (irreversible).

Solution:

a) This is a reversible process and constant temperature implies that $\Delta\bar{U} = 0$. Also the enthalpy change for an ideal gas depends only on temperature $\Delta\bar{H} = 0$. By using the 1st law and the expression for reversible expansion (see lecture notes), we get:

$$w_{rev} = -RT\ln\left(\frac{V_2}{V_1}\right) = -RT\ln\left(\frac{P_2}{P_1}\right) = -q_{rev}$$

By plugging in the values, we get $w_{rev} = -5.71$ kJ mol^{-1} and $q_{rev} = 5.71$ kJ mol^{-1}. Now the definition of entropy gives the entropy change:

$$\Delta\bar{S} = \frac{q_{rev}}{T} = 19.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

b) Irreversible process (free expansion). No external pressure – no work done ($w = 0$). Thus by the first law $q = 0$ (i.e. no heat exchanged with the surroundings) since $\Delta\bar{U} = 0$ and $\Delta\bar{H} = 0$. Entropy depends only on the endpoints of the path and hence $\Delta\bar{S} = \frac{q_{rev}}{T} = 19.1$ J K^{-1} mol^{-1}, where q_{rev} is from part a). Note that only reversible paths can be used in calculating entropy!

c) Isolated system, which here means that "system + surroundings" is isolated from the rest of the world. For a reversible process we have $dS_{tot} = dS_{syst} + dS_{surr} = 0$. For the system we have:

$$dS_{syst} = \frac{dq_{rev}}{T} \text{ and for the surroundings } dS_{surr} = -\frac{dq_{rev}}{T}$$

Since temperature is constant, $\Delta U = 0$ and $\Delta H = 0$. Therefore:

$$q_{rev} = -w = RT\ln\left(\frac{P_2}{P_1}\right) \text{ (from previous calculations)}$$

Thus $\Delta S_{syst} = R\ln(P_2/P_1)$ and $\Delta S_{surr} = -R\ln(P_2/P_1)$. Thus the total change of entropy (system + surroundings) is zero. Also $q_{tot} = q_{sys} + q_{surr} = RT\ln(P_2/P_1) - RT\ln(P_2/P_1) = 0$. For the same reason, the total work $w_{tot} = w_{sys} + w_{surr} = 0$. Note that the system + surroundings is isolated from the rest of the world and therefore the total change in heat (q_{tot}) and work (w_{tot}) must clearly be zero.

d) If we want to calculate the entropy change for the system, we need a reversible path for the calculation. Above this was done: $\Delta S_{syst} = R\ln(P_2/P_1)$. In free expansion, no work is done, $w_{sys} = 0$ (and $w_{surr} = 0$). Since $\Delta U = w_{sys} + q_{sys}$ and $\Delta U = 0$, $q_{sys} = 0$ as well (also then $q_{surr} = 0$). Thus the system is not interacting with the surroundings at all in this process. This means that the entropy of the surroundings does not change either, $\Delta S_{surr} = 0$. The total entropy is then $\Delta S_{tot} = \Delta S_{syst} + \Delta S_{surr} = R\ln(P_2/P_1) = 19.1$ J K^{-1} mol^{-1}.

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9. One mole of gas A at 1 bar and one mole of gas B at 2 bar are separated by a partition and surrounded by a heat reservoir (i.e. the temperature is constant). When the partition is withdrawn, how much does the entropy change? Both gases behave according to the ideal gas law. Hint: consider the calculation in three steps: (I) the initial entropy difference from standard state, (II) change in entropy due to expansion/compression of gases at constant temperature and finally (III) entropy change due to mixing of the gases.

Solution:

Note that the pressures of the two gases are different and thus the results in the lecture notes cannot be directly applied.

I The initial (i.e. before mixing) entropies for the gases are:

$$S_A = S_A^\circ - nR\ln\left(\frac{P_A^{ini}}{P_A^\circ}\right) = S_A^\circ - nR\ln\left(\frac{1\text{ bar}}{1\text{ bar}}\right) = S_A^\circ$$

$$S_B = S_B^\circ - nR\ln\left(\frac{P_B^{ini}}{P_B^\circ}\right) = S_B^\circ - nR\ln(2)$$

II Let both gases expand from their initial pressures to the final pressure at constant temperature. This changes entropy of both gases according to:

$$S_A = S_A^\circ - nR\ln\left(\frac{P_{total}}{P_A^\circ}\right) \text{ and } S_B = S_B^\circ - nR\ln\left(\frac{P_{total}}{P_B^\circ}\right)$$

where P_{total} is the final pressure after mixing. The final volume after mixing is:

$$V_{total} = V_A + V_B = \frac{nRT}{P_A} + \frac{nRT}{P_B} = \frac{nRT}{P_A} + \frac{nRT}{2P_A} = \frac{3nRT}{2P_A}$$

The total pressure after mixing is then:

$$P_{total} = \frac{2nRT}{V_{total}} = \frac{4}{3}P_A = \frac{4}{3}\text{ bar}$$

The entropy change due to expansion for both gases is:

$$S_A = S_A^\circ - nR\ln\left(\frac{4}{3}\right) \text{ and } S_B = S_B^\circ - nR\ln\left(\frac{4}{3}\right)$$

Combining 1 and 2, we have: $\Delta S_A = -n_A R\ln\left(\frac{4}{3}\right)$ and $\Delta S_B = -n_B R\left(\ln\left(\frac{4}{3}\right) - \ln(2)\right)$.

III Finally we must include the entropy change due to mixing ($n = 1$):

$$\Delta_{mix}S = -R\ln\left(\frac{1\text{ mol}}{2\text{ mol}}\right) - R\ln\left(\frac{1\text{ mol}}{2\text{ mol}}\right) = -2R\ln\left(\frac{1}{2}\right)$$

The total entropy change is then ("1 + 2 + 3"):

$$\Delta S_{total} = \Delta S_A + \Delta S_B + \Delta S_{mix} = -2R\ln\left(\frac{4}{3}\right) + R\ln(2) - 2R\ln\left(\frac{1}{2}\right)$$

$$= 12.51\text{ J K}^{-1}\text{ mol}^{-1}$$

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10. Calculate the change in molar entropy of aluminum that is heated from 600 ° to 700 °C. The melting point of aluminum is 660 °C, the heat of fusion is 393 J g^{-1} (the molar mass for aluminum is 27 g mol^{-1}), and the heat capacities at constant pressure of the solid and the liquid may be taken as 31.8 J K^{-1} mol^{-1} and 34.4 J K^{-1} mol^{-1} (independent of temperature), respectively.

Solution:

Note that 600 °C is 873 K, 660 °C is 933 K, and 700 °C is 973 K. Use the following equation (see lecture notes):

$$\Delta\bar{S} = \int\limits_{T_{initial}}^{T_{fusion}} \frac{C_P(s)}{T}dT + \frac{\Delta H_{fusion}}{T_{fusion}} + \int\limits_{T_{fusion}}^{T_{final}} \frac{C_P(l)}{T}dT$$

$$= C_P(s)\ln\left(\frac{T_{fusion}}{T_{initial}}\right) + \frac{\Delta H_{fusion}}{T_{fusion}} + C_P(l)\ln\left(\frac{T_{final}}{T_{fusion}}\right)$$

$$= (31.8\text{ J K}^{-1}\text{ mol}^{-1})\ln\left(\frac{933\text{ K}}{873\text{ K}}\right) + \frac{(27\text{ g mol}^{-1})(393\text{ J g}^{-1})}{933\text{ K}}$$

$$+(34.3\text{ J K}^{-1}\text{ mol}^{-1})\ln\left(\frac{973\text{ K}}{933\text{ K}}\right) = 19.92\text{ J K}^{-1}\text{ mol}^{-1}$$

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11. Steam is condensed at 100 °C, and the water is cooled to 0 °C and frozen to ice. What is the molar entropy change of the water? Consider that the average specific heat of liquid water is 4.2 J K^{-1} g^{-1} (the molar mass of water is 18.016 g mol^{-1}). The enthalpy of vaporization at the boiling point and the enthalpy of fusion at the freezing point are 2258.1 J g^{-1} and 333.5 J g^{-1}, respectively.

    Solution:

    Use the same cycle as in the previous problem (note that the cycle goes from high temperature to low temperature and thus the signs are reversed!):

$$\Delta\bar{S} = -\frac{\Delta H_{vap}}{T_{vap}} - \int\limits_{273.15\text{ K}}^{373.15\text{ K}} \frac{C_P(l)}{T}dT - \frac{\Delta H_{fus}}{T_{fus}} = -\frac{\left(2258.1\text{ J g}^{-1}\right)\left(18.016\text{ g mol}^{-1}\right)}{373.15\text{ K}}$$

$$- \left(4.2\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \times \left(18.016\ \text{g mol}^{-1}\right) \times \ln\left(\frac{373.15\ \text{K}}{273.15\ \text{K}}\right)$$

$$- \frac{\left(333.5\ \text{J g}^{-1}\right)\left(18.016\ \text{g mol}^{-1}\right)}{273.15\ \text{K}} = -154.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

12. Calculate the increase in the molar entropy of nitrogen when it is heated from 25 °C to 1000 °C at constant pressure with: $\bar{C}_P = 26.9835 + 5.9622 \times 10^{-3} T - 3.377 \times 10^{-7} T^2$ in J K^{-1} mol^{-1}.

    Solution:

    Nitrogen is gaseous in the temperature range. The entropy change is then given by:

$$\Delta \bar{S} = \int_{298.15\ \text{K}}^{1273.15\ \text{K}} \frac{C_P(g)}{T} dT = \Big/_{298.15\ \text{K}}^{1273.15\ \text{K}} \left(26.9835 \ln(T) + 5.9622 \times 10^{-3} T - \frac{3.377 \times 10^{-7}}{2} T^2\right)$$

$$= 44.73\ \text{J K}^{-1}\ \text{mol}^{-1}$$