Chem 338

Homework Set #4 solutions September 25, 2001

From Atkins: 4.2, 4.4, 4.6, 4.12, 4.18, 4.19, 4.22

4.2) Suppose you put a cube of ice of mass 100 g into glass of water at just above 0ºC. When the ice melts, about 33 kJ of energy is absorbed from the surroundings as heat. What is the change in entropy of (a) the sample (the ice), (b) the surroundings (the glass of water) ?

a) $\Delta S^o_{sys} = \dfrac{+33 \text{ kJ}}{273} = +0.12 \text{ kJ K}^{-1}$

b) $\Delta S^o_{surr} = \dfrac{-33 \text{ kJ}}{273} = -0.12 \text{ kJ K}^{-1}$

4.4) Calculate the change in entropy of 100 g of ice at 0ºC as it is melted, heated to 100ºC, and then vaporized at that temperature. Suppose that the changes are brought about by a heater that supplies heat at a constant rate, and sketch a graph showing (a) the change in temperature of the system, (b) then enthalpy of the system, (c) the entropy of the system as a function of time.

$$100 \text{ g } H_2O(s)\ 0°C \xrightarrow{\Delta S_1^o} H_2O(l)\ 0°C \xrightarrow{\Delta S_2^o} H_2O(l)\ 100°C \xrightarrow{\Delta S_3^o} H_2O(g)\ 100°C$$

amount of ice: $n = 100 \text{ g} \times \dfrac{1 \text{ mol}}{18.015 \text{ g}} = 5.5509 \text{ mol}$

$$\Delta S_1^o = \frac{q_{rev}}{T} = \frac{n\Delta H^o_{fus}}{T} = \frac{(5.5509)(6.01)}{273.15} = 0.12213 \text{ kJ/K}$$

$$\Delta S_2^o = nC_{p,m} \ln\frac{T_f}{T_i} = (5.5509)(0.07529)\ln\frac{373.15}{273.15} = 0.13038 \text{ kJ/K}$$

$$\Delta S_3^o = \frac{n\Delta H^o_{vap}}{T} = \frac{(5.5509)(40.7)}{373.15} = 0.60544 \text{ kJ/K}$$

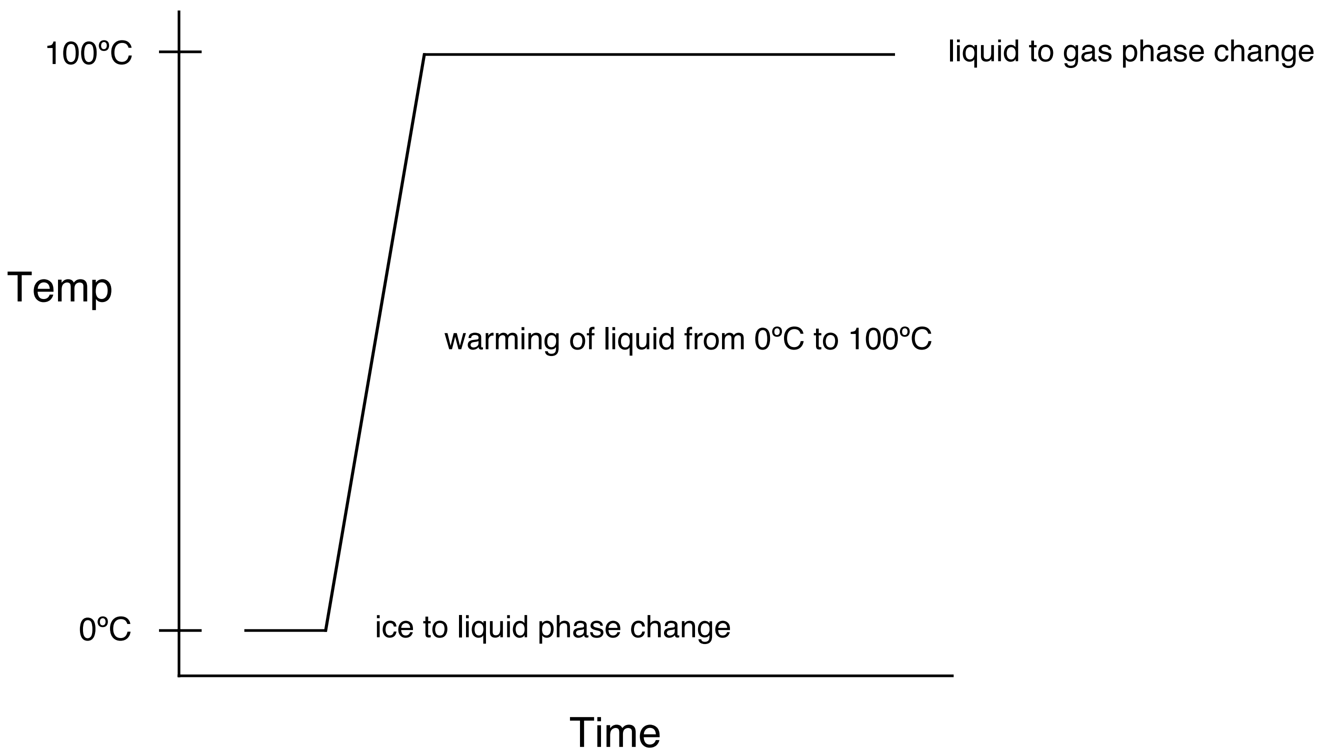
$$\Delta S^o_{total} = \Delta S_1^o + \Delta S_2^o + \Delta S_3^o = 0.858 \text{ kJ/K} = 860 \text{ J/K}$$

Total heat input into the system:

$$q = \Delta H^o = n\Delta H^o_{fus} + nC_{p,m}\Delta T + n\Delta H^o_{vap}$$
$$= 33.361 + 41.793 + 225.92 = 301 \text{ kJ}$$

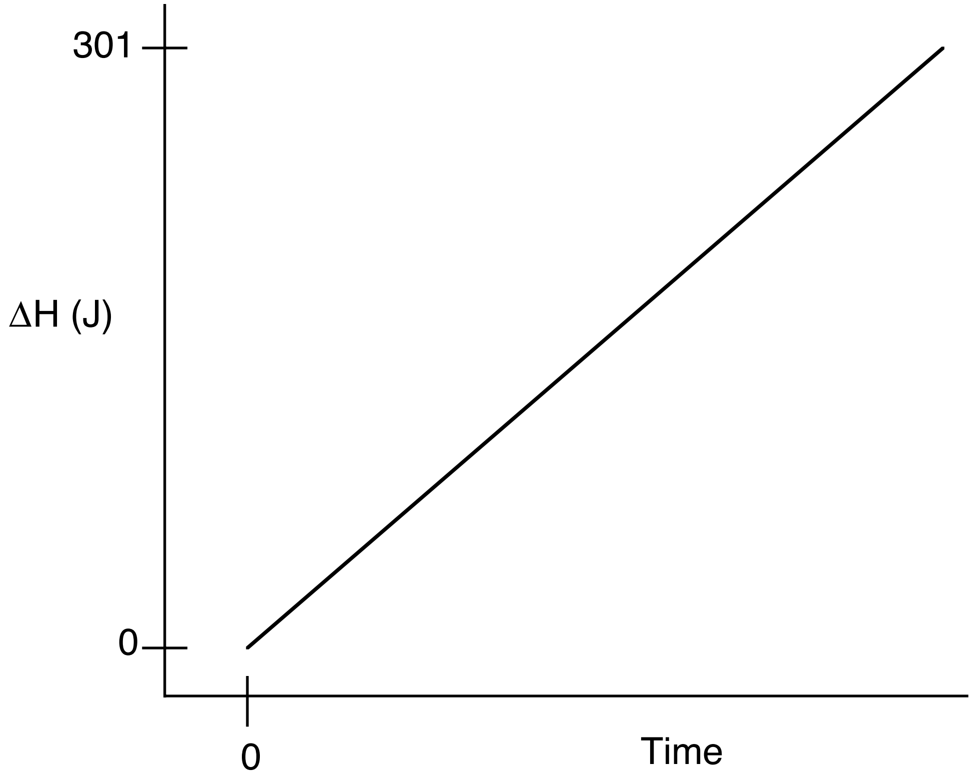
For a constant rate of heat input into the system:

<u>Temperature vs. time</u> (as in the last homework set)

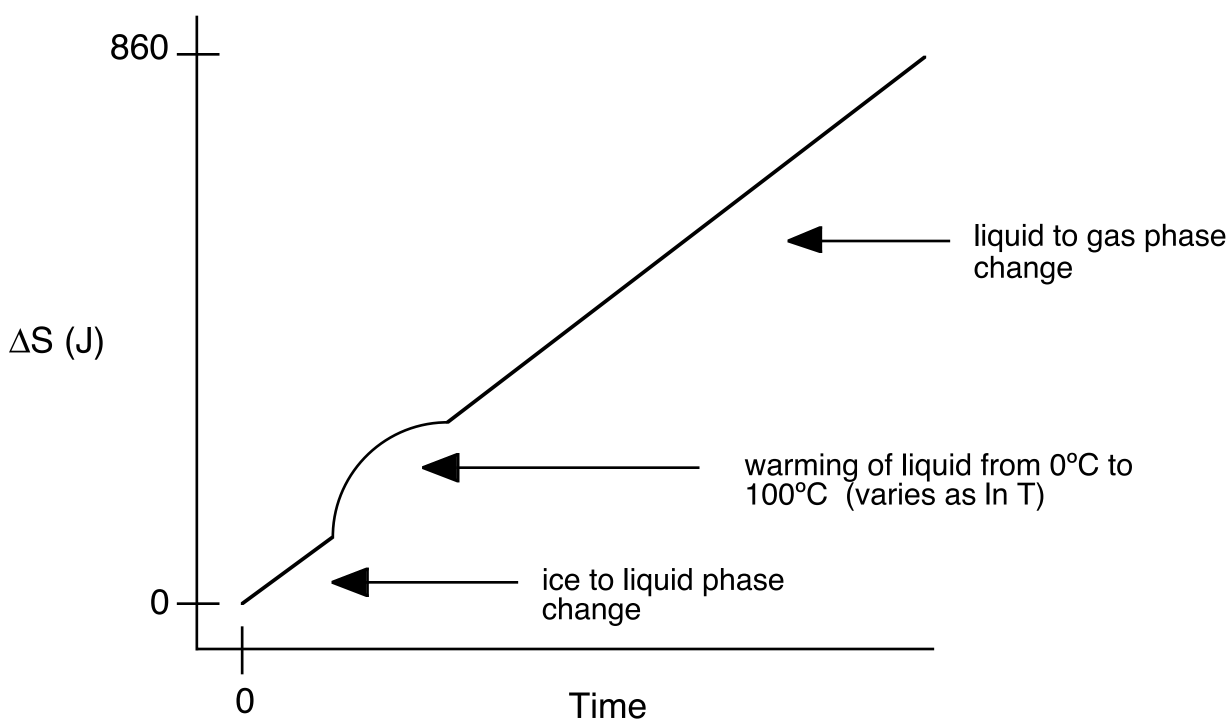


Enthalpy vs. time

(note: $q = \Delta H$ and q is being delivered at a constant rate)



Entropy vs. time



4.6) A sample of carbon dioxide that initially occupies 15.0 L at 250 K and 1.00 atm is compressed isothermally. Into what volume must the gas be compressed to reduce its entropy by 10.00 J K^{-1} ?

First calculate the number of moles of gas:

$$n = \frac{pV}{RT} = \frac{(1.00)(15.0)}{(0.0820578)(250)} = 0.7312 \text{ mol}$$

For the isothermal expansion/compression of a perfect gas:

$$\Delta S^o = nR \ln \frac{V_f}{V_i}$$

Solving for V_f:

$$V_f = V_i e^{\Delta S / nR}$$

For an entropy change of –10.0 J/K :

$$\begin{aligned} V_f &= (15.0) e^{-10.0 / (0.7312)(8.31451)} \\ &= 2.90 \text{ L} \end{aligned}$$

4.12) Calculate the change in entropy when 100 g of water at 80ºC is poured into 100 g of water at 10ºC in an insulated vessel given that $C_{p,m}$ = 75.5 J K^{-1} mol^{-1}.

We first need to find the final temperature. Since the amounts of hot and cold water are the same, the final temp is just the average of the initial temperatures: (80 + 10)/2 = 45ºC.

More rigorously, this is obtained by noting that the heat lost by the hot water is exactly equal to the heat gained by the cold water since the container is insulated:

$$q_{\text{lost by hot water}} = -q_{\text{gained by cold water}}$$

$$n_h C_{p,m} (T_f - 353) = -n_c C_{p,m} (T_f - 283)$$

and thus, $T_f = 318$ K (45°C) since $n_h = n_c$

Since entropy is a state function we can break down this process into two steps, the cooling of the hot water and the heating of the cold water:

$$\Delta S = \Delta S_{hot} + \Delta S_{cold}$$
$$= n_h C_{p,m} \ln\frac{318}{353} + n_c C_{p,m} \ln\frac{318}{283}$$

In each case, the amount of water is: $n = 100 \text{ g} \times \dfrac{1 \text{ mol}}{18.015 \text{ g}} = 5.5509 \text{ mol}$

$$\Delta S = (5.5509)(75.5)\left[-0.1044 + 0.1166\right] = 5.11 \text{ J/K}$$

4.18) Calculate the standard reaction entropy at 298 K of

(a) $2CH_3CHO(g) + O_2(g) \rightarrow 2CH_3COOH(l)$

In each case, ΔS_r^o is given by $\sum\limits_{prod} \nu_p S_m^o - \sum\limits_{reac} \nu_r S_m^o$

$$\Delta S_r^o = 2(159.8) - \left[2(250.3) + (205.138)\right] = -386.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) $2AgCl(s) + Br_2(l) \rightarrow 2AgBr(s) + Cl_2(g)$

$$\Delta S_r^o = 2(107.1) + (223.07) - \left[2(96.2) + (152.23)\right] = 92.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

(c) $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$

$$\Delta S_r^o = (146.0) - \left[(76.02) + (223.07)\right] = -153.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

(d) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$$\Delta S_r^o = (-112.1) + (33.150) - \left[(41.63) + (-99.6)\right] = -21.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

(e) $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

$$\Delta S_r^o = 12(213.74) + 11(69.91) - \left[(360.2) + 12(205.138)\right] = 512.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

4.19) The constant-pressure molar heat capacities of linear gaseous molecules are approximately 7/2 R and those of nonlinear gaseous molecules are approximately 4R. Estimate the change in standard reaction entropy of the following two reactions when the temperature is increased by 10 K from 273 K at constant pressure.

(a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

This problem is analogous to the derivation of Kirchhoff's law for the determination of the temperature dependence of the enthalpy. Using this first reaction as an example, here is the path that we should consider:

$$
\begin{tikzcd}
2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) \arrow[r, "\Delta S^o_{283}"] \arrow[d, "\Delta S_1"', "\Delta S_2"] & 2\mathrm{H}_2\mathrm{O}(\mathrm{g}) \\
2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) \arrow[r, "\Delta S^o_{273}"] & 2\mathrm{H}_2\mathrm{O}(\mathrm{g}) \arrow[u, "\Delta S_3"']
\end{tikzcd}
$$

Where,

$$\Delta S_1 = nC_{p,m}^{lin} \ln\frac{273}{283} = 2(\tfrac{7}{2}R)\ln\frac{273}{283}$$

$$\Delta S_2 = nC_{p,m}^{lin} \ln\frac{273}{283} = (\tfrac{7}{2}R)\ln\frac{273}{283}$$

$$\Delta S_3 = nC_{p,m}^{non-lin} \ln\frac{283}{273} = 2(4R)\ln\frac{283}{273}$$

$$\Delta S^o_{283} = \Delta S_1 + \Delta S_2 + \Delta S^o_{273} + \Delta S_3$$

or, $\Delta S^o_{283} - \Delta S^o_{273} = \Delta S_1 + \Delta S_2 + \Delta S_3$

But we can write the sum of the three entropy terms as:

$$\Delta S_1 + \Delta S_2 + \Delta S_3 = \Delta_r C_p \ln\frac{283}{273}$$

where, $\Delta_r C_p = \sum_{prod} \nu_p C_{p,m}^{prod} - \sum_{reac} \nu_r C_{p,m}^{reac}$ (as in Kirchhoff's law)

$$\Delta_r C_p = 2(4R) - 2(\tfrac{7}{2}R) - (\tfrac{7}{2}R) = -2.5R = -20.786 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S^o_{283} - \Delta S^o_{273} = (-20.786)\ln\frac{283}{273} = -0.75 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

For this reaction,

$$\Delta_r C_p = C_p^{lin} + 2C_p^{non-lin} - \left[C_p^{non-lin} + 2C_p^{lin}\right]$$
$$= R\left(\tfrac{7}{2} + 8 - 4 - 7\right) = \tfrac{1}{2}R$$

$$\Delta S^o_{283} - \Delta S^o_{273} = (\tfrac{1}{2}R)\ln\frac{283}{273} = +0.15 \text{ J K}^{-1} \text{ mol}^{-1}$$

4.22) The change in Gibbs energy that accompanies the oxidation of $C_6H_{12}O_6(s)$ to carbon dioxide and water vapour at 25ºC is –2828 kJ/mol. How much glucose does a person of mass 65 kg need to consume to climb through 10 m?

$C_6H_{12}O_6(s) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

ΔG_r^o yields the maximum non-expansion work (like climbing),

work = mgh, for 65 kg through 10 m : work = (65)(9.81)(10) = 6376.5 J

$$\text{\# moles of glucose} = 6376.5 \times \frac{1 \text{ mol glucose}}{2828 \times 10^3 \text{ J}} = 2.25 \times 10^{-3} \text{ mol}$$

$$2.25 \times 10^{-3} \text{ mol} \times \frac{180.16 \text{ g}}{\text{mol}} = 0.41 \text{ g of glucose}$$