**Chem 338**

Homework Set #3 solutions September 18, 2001

From Atkins: 3.2, 3.5, 3.6, 3.10, 3.19, 3.22, 3.23, 3.25, 3.27

3.2) Calculate the heat required to evaporate 1.00 kg of water at (a) 25ºC, (b) 100ºC.

The process is: $H_2O(l) \rightarrow H_2O(g)$

$$1.00\times10^3 \text{ g} \times \frac{1 \text{ mol}}{18.016 \text{ g}} = 55.506 \text{ mol}$$

From Table 3.1, $\Delta H^o_{vap}(373.15\,\text{K}) = 40.7 \text{ kJ/mol}$

For 298.15 K, use heat of formation data at 298.15 K to obtain the enthalpy of the above reaction, which is equal to the enthalpy of vaporization:

$$\Delta H^o_{vap} = \Delta H^o_f(H_2O(g)) - \Delta H^o_f(H_2O(l))$$
$$= 44.01 \text{ kJ/mol}$$

(a) at 25ºC, $q = \Delta H = (55.506)(44.01) = 2.44 \times 10^3$ kJ

(b) at 100ºC, $q = (55.506)(40.7) = 2.26 \times 10^3$ kJ

3.5) Use the information in Tables 2.1 and 3.1 to calculate the total heat required to melt 100 g of ice at 0ºC, heat it to 100ºC, and then vaporize it at that temperature. Sketch a graph of temperature against time on the assumption that heat is supplied to the sample at a constant rate.

From the above tables:

$C_{p,m}(H_2O(l)) = 75.29$ kJ/mol

$\Delta H_{fus}(H_2O)$=6.01 kJ/mol at 0ºC

$\Delta H_{vap}(H_20)$=40.7 kJ/mol at 100ºC

$$n = 100 \text{ g } H_2O(s) \times \frac{1 \text{ mol}}{18.016 \text{ g}} = 5.5506 \text{ mol } H_2O(s)$$

The process we're interested in is:

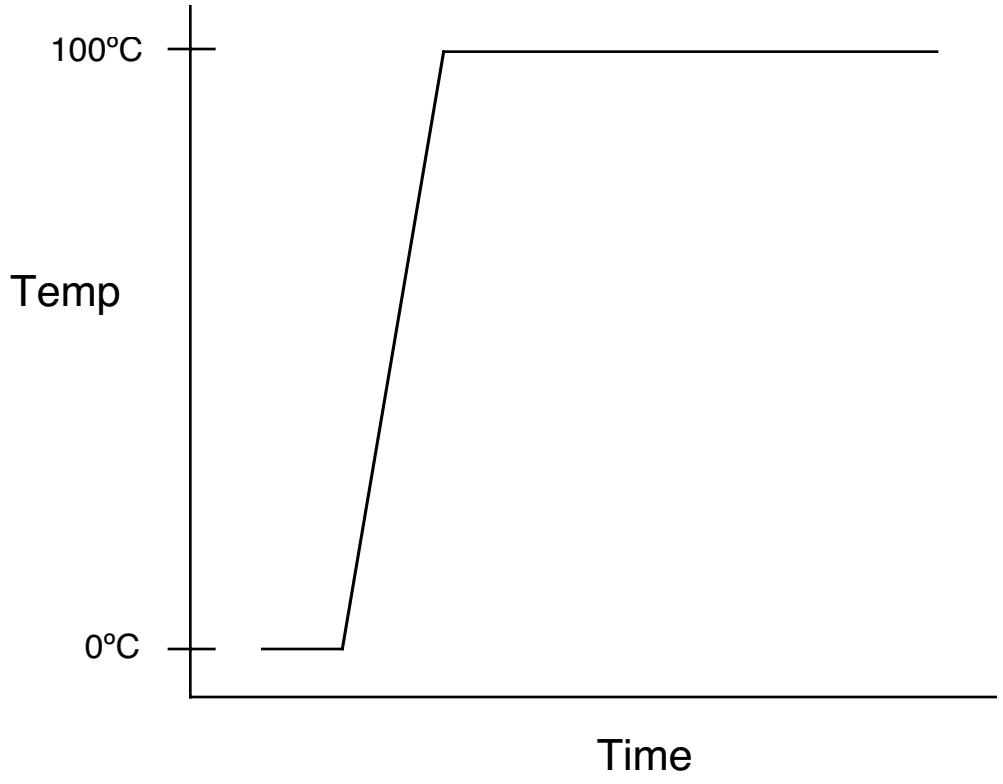
$H_2O(s)$, 0ºC $\rightarrow$ $H_2O(l)$, 0ºC $\rightarrow$ $H_2O(l)$, 100ºC $\rightarrow$ $H_2O(g)$, 100ºC

The total heat required is the sum of 3 enthalpy changes:

$$q = n\Delta H^o = n\Delta H^o_{fus} + nC_{p,m}\Delta T + n\Delta H^o_{vap}$$

$$= (5.5506)[6.01 + (0.07529)(100) + 40.7] = 301 \text{ kJ}$$

Assuming constant rate of heating (approximately to scale):




3.6) The enthalpy of sublimation of calcium at 25°C is 178.2 kJ/mol. How much energy (at constant temperature and pressure) must be supplied to 10.0 g of solid calcium to produce a gas composed of $Ca^{2+}$ ions and electrons:?

The overall process of interest is: $Ca(s) \rightarrow Ca^{2+}(g) + 2e^-$

But the path we will take is: $Ca(s) \rightarrow Ca(g) \rightarrow Ca^+(g) + e^- \rightarrow Ca^{2+}(g) + 2e^-$

The 1st step is just the enthalpy of sublimation, while the next two are $\Delta H_{ion,1}$ = 590 kJ/mol and $\Delta H_{ion,2}$ = 1150 kJ/mol (Table 3.2)

$$n = 10.0 \text{ g Ca(s)} \times \frac{1 \text{ mol}}{48.08 \text{ g}} = 0.249501 \text{ mol Ca(s)}$$

$$\Delta H = (0.249501)[(178.2 + 590 + 1150)] = 479 \text{ kJ}$$

3.10) The standard enthalpy of reaction for $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_20(l)$ is –3120 kJ/mol. (a) What is the standard enthalpy of combustion of ethane? (b) What is the change in enthalpy when 3.00 mol of $CO_2$ is formed in the reaction?

(a) The reaction as written above is identical to the combustion reaction, except that it is written for 2 moles of ethane rather than for one.

$$\text{Hence, } \Delta H_c^o = \frac{\Delta H_r^o}{2} = \frac{-3120}{2} = -1560 \text{ kJ / mol}$$

(b) for 3 moles of $CO_2$ produced, $\Delta H_r^o = \frac{3}{4}\Delta H_r^o = -2340$ kJ

3.19) The standard enthalpy of decomposition of the yellow complex $NH_3SO_2$ into $NH_3$ and $SO_2$ is +40 kJ/mol. Calculate the standard enthalpy of formation of $NH_3SO_2$.

The decomposition reaction refers to: $NH_3SO_2 \rightarrow NH_3(g) + SO_2(g)$

Using enthalpies of formation:

$$\Delta H_{decomp}^o = \Delta H_f^o(NH_3(g)) + \Delta H_f^o(SO_2(g)) - \Delta H_f^o(NH_3SO_2(g))$$

or,

$$\begin{aligned}\Delta H_f^o(NH_3SO_2(g)) &= \Delta H_f^o(NH_3(g)) + \Delta H_f^o(SO_2(g)) - \Delta H_{decomp}^o \\ &= (-46.11) + (-296.83) - (40) \\ &= -383 \text{ kJ / mol}\end{aligned}$$

3.22) The mass of a typical sugar (sucrose) cube is 1.5 g. Calculate the energy released as heat when a cube is burned in air. To what height could a person of mass 68 kg climb on the energy a cube provides assuming 20% of the energy is available for work?

$$n = 1.5 \text{ g sucrose} \times \frac{1 \text{ mol}}{342.30 \text{ g}} = 0.0043821 \text{ mol}$$

$q = n\Delta H_c^o = (0.0043821)(-5645) = -24.74$ kJ released

20% of this: (0.20)(–24.74) = 4.948 kJ available for work

$$w = mgh \quad \text{or} \quad h = \frac{4.948 \times 10^3 \text{ J}}{(68 \text{ kg})(9.81 \text{ m/s})} = 7.4 \text{ m} \quad \text{(better eat 2 or 3 ….)}$$

3.23) The standard enthalpy of combustion of propane gas is –2220 kJ/mol and the standard enthalpy of vaporization of the liquid is +15 kJ/mol. Calculate (a) the standard enthalpy and (b) the standard internal energy of combustion of the liquid.

The process of interest is: $C_3H_8(l) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

(a) Use the path: $C_3H_8(l) + 5O_2(g) \rightarrow C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

The first step is just the heat of vaporization of the liquid and the 2nd is the heat of combustion of the gas:

$$\Delta H_c^o(C_3H_8(l)) = 15 + (-2220) = -2205 \text{ kJ/mol}$$

(b) The internal energy is related to the enthalpy by

$\Delta U = \Delta H - \Delta(pV) = \Delta H - \Delta(nRT) = \Delta H - RT\Delta n_g$, where $\Delta n_g$ is the change in the number moles of perfect gas in the process at constant T. In the combustion of the liquid, $\Delta n_g = 3 - 5 = -2$ moles (see overall reaction above)

$\Delta U_c^o = (-2205) - (-2)(8.31451 \times 10^{-3})(298.15) = -2200$ kJ/mol

3.25) Use the data in Appendix 1 to calculate the standard enthalpies of the following reactions:

in each case use $\Delta H_r^o = \sum_{prod} \nu_p \Delta H_f^o(prod) - \sum_{reac} \nu_r \Delta H_f^o(reac)$

(a) $2NO_2(g) \rightarrow N_2O_4(g)$

(9.16 kJ/mol) – 2(33.18 kJ/mol) = –57.20 kJ/mol

(b) $NO_2(g) \rightarrow 1/2\ N_2O_4(g)$

this is just 1/2 that of (a), (–57.20 kJ/mol)/2 = –28.60 kJ/mol

(c) $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

(90.25) + 2(–207.36) – 3(33.18) – (–285.83) = –138.18 kJ/mol

(d) Cyclopropane(g) → propene(g)

(20.42) – (53.30) = –32.88 kJ/mol

(e) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

note: HCl and NaOH are strong acids and bases and are completely dissociated in water.

$(H_2O) + (Na^+ + Cl^-) – (H^+ + Cl^-) – (Na^+ + OH^-)$

(–285.83) + (–240.12 – 167.16) – (0 – 167.16) – (–240.12 – 229.99) = –55.84 kJ/mol

3.27) Use the information in Appendix 1 to predict the standard reaction enthalpy of $2NO_2(g) \rightarrow N_2O_4(g)$ at 100ºC from its value at 25ºC.

Kirchhoff's "Law" : $\Delta H_r^o(T_2) = \Delta H_r^o(T_1) + \Delta_r C_p \Delta T$

For $\Delta H_r^o(298)$, use result from 3.25(a) : –57.20 kJ/mol

From Appendix 1,

$C_{p,m}(N_2O_4) = 77.28\ J\ K^{-1}\ mol^{-1}$ and $C_{p,m}(NO_2) = 37.20\ J\ K^{-1}\ mol^{-1}$

$\Delta_r C_p = 77.28 – 2(37.20) = 2.88\ J\ K^{-1}\ mol^{-1}$

$\Delta H_r^o(298) = –57.20 + (2.88 \times 10^{-3})(373 – 298) = –56.98\ kJ/mol$