Chemistry 240 Semester 01-2009
Homework for Submission #6

Answer the following questions and submit them for marking on or before Thursday 2nd April in the chemistry drop box. If any answers show evidence of copying, the whole exercise will attract zero marks.

1) a) Given that $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ and $\Delta G^{\ominus} = -RT\ln K$, show that

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where K_1 and K_2 are the equilibrium constants for a given reaction at temperatures T_1 and T_2 respectively, assuming that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are constant over the temperature range T_1 to T_2. (This result is known as the Van't Hoff equation.)

b) Consider

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g),\ \Delta H^{\ominus} = -197.8\ \text{kJ},\ K = 4.0 \times 10^{24}\ \text{at}\ 298\ \text{K}$$

Estimate the value of K at 500 K.

c) Compare your answer to (b) with the experimental value of 2.5×10^{10} and explain the discrepancy.

2) a) Write down the equilibrium expression for

$$C_6H_6(l) \rightleftharpoons C_6H_6(g),\ \Delta H^{\ominus} = \Delta H^{\ominus}_{vap},$$

in terms of partial pressure.

b) Use your relationship from (a), together with the Van't Hoff equation, to derive the *Clapeyron-Clausius* equation,

$$\ln\frac{P_2}{P_1} = \frac{\Delta H^{\circ}_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

c) Given that the *normal boiling point* of benzene, C_6H_6, is 80.0°C, and its standard molar enthalpy of vaporisation, $\Delta H^{\ominus}_{vap}$, is +33.9 kJ mol^{-1}, estimate its vapour pressure at 25°C.

3) The thermal decomposition of methoxymethane at 510°C, $(CH_3)_2O$, is a first-order process:

$$(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

a) Write down the differential rate equation for the reaction.

b) Derive the integrated rate equation.

c) Derive a relationship between the pressure of the reaction mixture and the concentration of methoxymethane. Assume ideal behaviour.

d) How would you determine the rate constant for the reaction from measured values of pressure at various times?

e) Define the term "half-life", ($t_{½}$) and show how it is related to the rate constant, k.

f) Why is the concept of half-life particularly useful for first-order reactions?

g) A piece of wood from a living tree, which is slightly radioactive due to the presence of carbon-14, gives 15.0 counts[1] per minute per gram of carbon. A piece of wood from an ancient axe-head found in a cave gives 8.5 counts per minute per gram of carbon under the same conditions. Estimate the age of the axe-head. (The half-life of C is 5600 years.)

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[1] The "counts per minute" shows the number of disintegrations of carbon-14 atoms detected every minute by a Geiger counter or similar. It is proportional to the concentration of carbon-14 in the sample and decreases gradually with time as the carbon-14 decomposes to nitrogen-14 via β decay (i.e. the emission of an energetic electron). Radioactive decay is a first-order process.