

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

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

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

Solution

$$\Delta G^\ominus = -RT \ln K$$

But $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ at constant temperature

$$\therefore -RT \ln K = \Delta H^\ominus - T\Delta S^\ominus$$

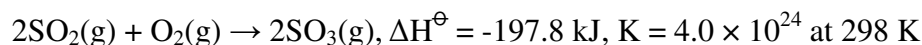
$$\therefore \ln K = \frac{-1}{RT} (\Delta H^\ominus - T\Delta S^\ominus) = \frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT} \text{ or at two different temperatures :}$$

$$\ln K_1 = \frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT_1} \text{ and } \ln K_2 = \frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT_2}$$

$$\therefore \ln K_2 - \ln K_1 = \left(\frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT_2} \right) - \left(\frac{\Delta S^\ominus}{R} - \frac{\Delta H^\ominus}{RT_1} \right) = \frac{1}{R} \left(\frac{\Delta H^\ominus}{T_1} - \frac{\Delta H^\ominus}{T_2} \right) = \frac{\Delta H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

b) Consider



Estimate the value of K at 500 K.

Solution

Substituting, we have

$$\ln \frac{K_2}{4.0 \times 10^{24}} = \frac{-197.8 \times 10^3}{8.31} \left(\frac{1}{298} - \frac{1}{500} \right)$$

$$\therefore \ln K_2 = \frac{-197.8 \times 10^3}{8.31} \left(\frac{1}{298} - \frac{1}{500} \right) + \ln(4.0 \times 10^{24}) = -24.38$$

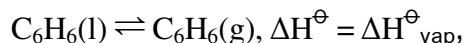
$$\therefore K_2 = 3.869 \times 10^{10} = \underline{\underline{3.9 \times 10^{10}}} \text{ to 2 sig. figs.}$$

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

Answer

The calculated value is in the right order of magnitude, but differs considerably because ΔH and ΔS vary with temperature.

2) a) Write down the equilibrium expression for



in terms of partial pressure.

Solution

$$K = P_{\text{C}_6\text{H}_6}$$

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

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Solution

Since $K = P_{\text{C}_6\text{H}_6}$, at T_1 , $K = K_1 = P_1$ and at T_2 , $K = K_2 = P_2$. ΔH is $\Delta H_{\text{vap}}^{\ominus}$, since we are dealing with an evaporation under standard conditions. Substituting for K_1 , K_2 and ΔH^{\ominus} in Van't Hoff's equation gives us:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

Solution

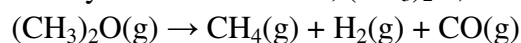
Since this is the normal boiling point, when $T = 80.0^\circ\text{C}$, $P = 1 \text{ atm}$, and so:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \text{ becomes}$$

$$\ln \frac{P_2}{1} = \frac{33.9 \times 10^3}{R} \left(\frac{1}{273 + 80} - \frac{1}{273 + 25} \right) = -2.133$$

$$\therefore P_2 = \underline{\underline{0.1185 \approx 0.12 \text{ atm} = 90 \text{ mmHg} = 1.2 \times 10^4 \text{ Pa to 2 sig. figs.}}}$$

- 3) The thermal decomposition of methoxymethane at 510°C , $(\text{CH}_3)_2\text{O}$, is a first-order process:



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

Solution

$$\frac{d[(\text{CH}_3)_2\text{O}]}{dt} = -k[(\text{CH}_3)_2\text{O}]$$

- b) Derive the integrated rate equation.

Solution

$$\text{Let } [(\text{CH}_3)_2\text{O}] = x$$

$$\therefore \frac{dx}{dt} = -kx$$

$$\therefore \frac{dx}{x} = -k dt$$

$$\therefore \int_{x_0}^{x_t} \frac{dx}{x} = -k \int_0^t dt$$

$$\therefore [\ln x]_{x_0}^{x_t} = -k[t]_0^t$$

$$\therefore \ln x_t - \ln x_0 = -k(t - 0)$$

$$\therefore \ln x_t = \ln x_0 - kt$$

This can be expressed in various other forms such as $\ln \frac{x_0}{x_t} = kt$.

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

Solution

| | (CH ₃) ₂ O(g) | CH ₄ (g) | H ₂ (g) | CO(g) |
|--|--|---------------------|--------------------|-------|
| Initial | P ₀ | 0 | 0 | 0 |
| Change | -y | +y | +y | +y |
| Final (after some reaction) | P _t = P ₀ - y | y | y | y |
| Total pressure, P _{tot} , after some reaction | $P_{tot} = P_0 + 2y$ $\therefore y = \frac{1}{2}(P_{tot} - P_0)$ | | | |

The partial pressure of (CH₃)₂O after some reaction is P_t = P₀ - y. But y = 1/2(P_{tot} - P₀) and so P_t = P_{tot} - 1/2(P_{tot} - P₀) = 1/2(P_{tot} + P₀)

Since PV = nRT for an ideal gas or gas mixture,

$$\therefore \text{Concentration, } \frac{n}{V} = \frac{P}{RT} = \frac{\frac{1}{2}(P_{tot} + P_0)}{RT}$$

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

Solution

For a given temperature it can be seen that concentration of methoxymethane is proportional to (P_{tot} + P₀)

and substituting in $\ln \frac{x_0}{x_t} = kt$ we have:

$$\ln \frac{P_0}{P_{tot} + P_0} = kt$$

A plot of $\ln \frac{P_0}{P_{tot} + P_0}$ against t should give a straight line through the origin of slope k.

- e) Define the term “half-life”, (t_{1/2}) and show how it is related to the rate constant, k.

Answer

The half-life for a reaction is the time required for a reactant concentration to drop to one half of its initial value.

Since $\ln \frac{x_0}{x_t} = kt$ and at the half-life, t = t_{1/2} and x_t = 1/2 x₀. Hence:

$$\ln \frac{x_0}{\frac{1}{2}x_0} = kt_{1/2}$$

$$\therefore \ln(2) = kt_{1/2}$$

$$\therefore k = \frac{\ln 2}{t_{1/2}}$$

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

Answer

For first order reactions the half-life is independent of the initial concentration of the reactant.

g) A piece of wood from a living tree, which is slightly radioactive due to the presence of carbon-14, gives 15.0 counts¹ per minute per gram of carbon. A piece of wood from an ancient axe-handle 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.)

Solution

For a first order reaction:

$$k = \frac{\ln 2}{t_{1/2}}$$

$$\therefore k = \frac{\ln 2}{5600} = 1.238 \times 10^{-4} \text{ yr}^{-1}$$

$$\text{But } \ln \frac{x_0}{x_t} = kt$$

$$\therefore \ln \frac{15.0}{8.5} = 1.238 \times 10^{-4} t$$

$$\therefore t = \frac{\ln\left(\frac{15}{8.5}\right)}{1.238 \times 10^{-4}} = 4.589 \times 10^3 = \underline{\underline{4.6 \times 10^3 \text{ yr}}}$$

This value represents the age of the axe-head i.e. about 4600 years.

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.