[Solutions]

CHEM 104
PLI 27
Friday, July 8, 2016

Chapter 14

1. Consider the following reaction between nitrogen dioxide and carbon monoxide:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

The initial rate of the reaction was measured at several different concentrations of the reactants with the following results:

$[NO_2]$ (M)	[CO] M	Initial rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0082
0.20	0.20	0.0083
0.40	0.10	0.033

(×2 → ×4; ×2 → ×1)

From the data, determine the rate law and the rate constant (k) for the reaction.

The data indicate that the reaction is second order for NO_2 and zero order for CO. $\boxed{Rate = k[NO_2]^2}$

$k = \frac{rate}{[NO_2]^2} = \frac{0.0021\ M/s}{(0.10\ M)^2} = \boxed{0.21\ M^{-1}s^{-1}}$ → units of k are $\frac{L}{mol}\cdot\frac{1}{s}$

2. Consider the equation for the decomposition of SO_2Cl_2: $SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$

The concentration of SO_2Cl_2 was monitored at a fixed temperature as a function of time during the decomposition. The reaction was determined to be first order and has a rate constant of $2.90 \times 10^{-4}\ s^{-1}$. If the reaction is carried out at the same temp., and the initial concentration of SO_2Cl_2 is 0.0225 M, what will the SO_2Cl_2 concentration be after 865 sec?

Rate is first order: rate $= k[SO_2Cl_2] = 2.90\times10^{-4}\frac{1}{s}[SO_2Cl_2]$

Integrated rate law: $\ln[SO_2Cl_2]_t = -kt + \ln[SO_2Cl_2]_0$

$\ln[SO_2Cl_2]_t = -2.90\times10^{-4}\frac{1}{s}(865\,s) + \ln(0.0225\,M)$

$\ln[SO_2Cl_2]_t = -4.05 \rightarrow [SO_2Cl_2] = e^{-4.05} = \boxed{0.0175\ M}$

3. The solubility of nitrogen gas in water is 821 μmol/L at 0°C when N_2 pressure above the water is 0.790 atm. (a) What is the Henry's Law constant for N_2 in units of mol/L•atm?

$S_g = k_H P_g \rightarrow k_H = \frac{S_g}{P_g} = \frac{821\times10^{-6}\ mol/L}{0.790\ atm} = \boxed{1.04\times10^{-3}\ \frac{mol}{L\cdot atm}}$

(b) What is the solubility of N_2 in water when the partial pressure of nitrogen above the water is 1.10 atm at 0°C?

$S_g = k_H P_g = 1.04\times10^{-3}\frac{mol}{L\cdot atm}(1.10\ atm) = \boxed{1.14\times10^{-3}\ \frac{mol}{L}}$

4. A reaction in which A, B, and C react to form products is first order in A, second order in B, and zero order in C.

a. Write a rate law for the reaction $rate = k[A][B]^2$

b. What is the overall order of the reaction? third order

c. By what factor does the rxn rate change if [A] is doubled and the rest stay constant? 2

d. By what factor does the rxn rate change if [B] is doubled and the rest stay constant? 4

e. By what factor does the rxn rate change if [C] is doubled and the rest stay constant? 1 (no change)

f. By what factor does the rxn rate change if all three concentrations are doubled? 8

g. What are the units of the rate constant, k, for the reaction? $\frac{L^2}{mol^2} \cdot \frac{1}{s}$ or $M^{-2} s^{-1}$

(you just want the units of the rate to be M/s).

5. This reaction was monitored as a function of time: A→ B + C
A plot of ln[A] vs. time yields a straight line with slope -0.0045 s^{-1}. first order!

a. What is the value of the rate constant for this reaction at this temperature? $k = -slope = 0.0045 \frac{1}{s}$

b. Write the rate law for the reaction. $rate = 0.0045 \frac{1}{s} [A]$

c. What is the half-life? $t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.0045} = 154 \text{ s}$

d. If the initial concentration of A is 0.250 M, what will be the concentration after 225 s?
$\ln[A]_t = -kt + \ln[A]_0 = -0.0045 \frac{1}{s}(225 s) + \ln(0.250 M) = -2.40$
$[A]_t = e^{-2.40} = 0.0908 M$

6. Calculate the freezing point and boiling point of each aqueous solution, assuming complete dissociation of the solute. For water, K_{bp} = 0.512 °C/*m* and K_{fp} = 1.86 °C/*m*. $T_{fp} = 0°C$, $T_{bp} = 100°C$

a. 0.100 *m* K_2S in water

Freezing: $\Delta T_{fp} = K_{fp}(m \cdot i) = 1.86 °C/m (0.100 m)(3) = 0.558°C$ $T_{fp} = -0.558°C$

Boiling: $\Delta T_{bp} = K_{bp}(m \cdot i) = 0.512 °C/m (0.100 m)(3) = 0.1536°C$ $T_{bp} = 100.154°C$

b. 21.5 g of $CuCl_2$ in 4.50 x 10^2 g in water Calculate m: $21.5 g\, CuCl_2 \left(\frac{1 mol}{134.45 g}\right) / 0.450 kg\, H_2O = 0.355 m$

Freezing: $\Delta T_{fp} = K_{fp}(m \cdot i) = 1.86°C/m (0.355 m)(3) = 1.98°C$ $T_{fp} = -1.98°C$

Boiling: $\Delta T_{bp} = K_{bp}(m \cdot i) = 0.512°C/m (0.355 m)(3) = 0.546°C$ $T_{bp} = 100.546°C$

c. 5.5% $NaNO_3$, by mass, in water assume 100 g: $5.5 g\, NaNO_3 \left(\frac{1 mol}{84.99 g}\right) / 0.0945 kg\, H_2O = 0.685 M$

Freezing: $\Delta T_{fp} = K_{fp}(m \cdot i) = 1.86°C/m (0.685 m)(2) = 2.55°C$ $T_{fp} = -2.55°C$

Boiling: $\Delta T_{bp} = K_{bp}(m \cdot i) = 0.512°C/m (0.685 m)(2) = 0.701°C$ $T_{bp} = 100.701°C$