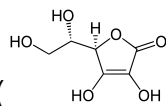


***Lots of problems are available. Do whichever ones give you the most trouble.***

### **Solutions & Colligative Properties**

A solution is prepared by mixing 1.00 g methanol ( $\text{CH}_3\text{OH}$ ) with 100.0 g of water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of methanol in this solution.



Is vitamin C ( ) miscible in water, hexane ( $\text{C}_6\text{H}_{12}$ ), or both? Explain your choice.

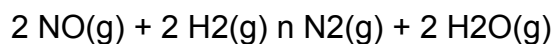
A 35.0-g sample of ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , is dissolved in 500.0 g of water. The vapor pressure of water at 32 °C is 35.7 mm Hg. What is the vapor pressure of the water–ethylene glycol solution at 32 °C? (Ethylene glycol is nonvolatile.) (Q13.25 from textbook)

The partial pressure of  $\text{O}_2$  in your lungs varies from 25 mm Hg to 40 mm Hg. What mass of  $\text{O}_2$  can dissolve in 1.0 L of water at 25 °C if the partial pressure of  $\text{O}_2$  is 40 mm Hg?  $K_{\text{H}}$  for  $\text{O}_2$  dissolved in  $\text{H}_2\text{O}$  at 25 °C is  $1.3 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{atm})$ . (Q13.19 from textbook).

*Challenge (review from lecture):* A 25.0 gram mixture of sucrose,  $C_{12}H_{22}O_{11}$ , and glucose,  $C_6H_{12}O_6$ , both non-volatile, non-electrolytes are dissolved in 500.0 g of water. The change in freezing point is  $0.500\text{ }^{\circ}\text{C}$ , and the  $K_f$  is  $1.86\text{ }^{\circ}\text{C/m}$ . What is the mass of glucose in the mixture? The mass of sucrose? (Molar mass of glucose is 180.2 g/mol. Molar mass of sucrose is 342.3 g/mol.)

## Kinetics

The reaction

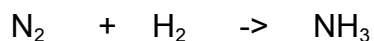


was studied at 904 °C, and the data in the table were collected:

| Reactant Concentration (mol/L) |                   | Rate of Appearance of $\text{N}_2$ (mol/L · s) |
|--------------------------------|-------------------|------------------------------------------------|
| [NO]                           | [H <sub>2</sub> ] |                                                |
| 0.420                          | 0.122             | 0.136                                          |
| 0.210                          | 0.122             | 0.0339                                         |
| 0.210                          | 0.244             | 0.0678                                         |
| 0.105                          | 0.488             | 0.0339                                         |

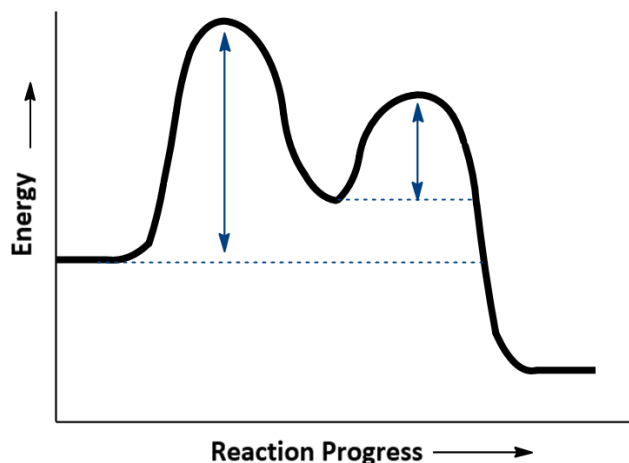
- (a) Determine the order of the reaction for each reactant.
- (b) Write the rate equation for the reaction.
- (c) Calculate the rate constant for the reaction
- (d) As an aside, what are the units of k for 0th, 1st, and 2nd order reactions?
- (e) Find the rate of appearance of N<sub>2</sub> at the instant when [NO] = 0.350 mol/L and [H<sub>2</sub>] = 0.205 mol/L.

Consider the following unbalanced chemical reaction:



If the H<sub>2</sub> is consumed at a rate of -0.75 M/s in this reaction, what is the rate at which NH<sub>3</sub> is produced (i.e.  $\Delta[\text{NH}_3]/\Delta t$ )?

Consider the following energy diagram showing a two step reaction:



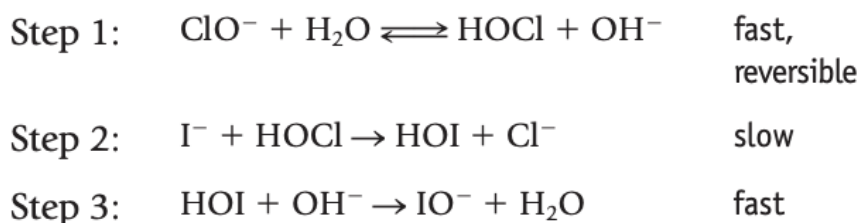
- What does the left arrow represent? What about the right?
- Is the first reaction exothermic or endothermic? What about the second reaction?
- Draw an double pointed arrow (like the ones on the diagram) representing the total energy of the first transition state.
- Draw another double pointed arrow representing the total energy of the intermediate.
- Draw another double pointed arrow representing the total  $\Delta H$  of the reaction.

97) The oxidation of iodide ion by the hypochlorite ion in the presence of hydroxide ions  $\text{I}^-(\text{aq}) + \text{ClO}^-(\text{aq}) \rightarrow \text{IO}^-(\text{aq}) + \text{Cl}^-(\text{aq})$  was studied at  $25^\circ\text{C}$ , and the following initial rates data (Y. Chia and R. E. Connick, Journal of Physical Chemistry, 1959, 63, 1518–1519) were collected:

| Experiment | Initial Concentrations (mol/L) |                      |                 | Initial Rate<br>(mol $\text{IO}^-/\text{L} \cdot \text{s}$ ) |
|------------|--------------------------------|----------------------|-----------------|--------------------------------------------------------------|
|            | $[\text{ClO}^-]$               | $[\text{I}^-]$       | $[\text{OH}^-]$ |                                                              |
| 1          | $4.0 \times 10^{-3}$           | $2.0 \times 10^{-3}$ | 1.0             | $4.8 \times 10^{-4}$                                         |
| 2          | $2.0 \times 10^{-3}$           | $4.0 \times 10^{-3}$ | 1.0             | $5.0 \times 10^{-4}$                                         |
| 3          | $2.0 \times 10^{-3}$           | $2.0 \times 10^{-3}$ | 1.0             | $2.4 \times 10^{-4}$                                         |
| 4          | $2.0 \times 10^{-3}$           | $2.0 \times 10^{-3}$ | 0.50            | $4.6 \times 10^{-4}$                                         |

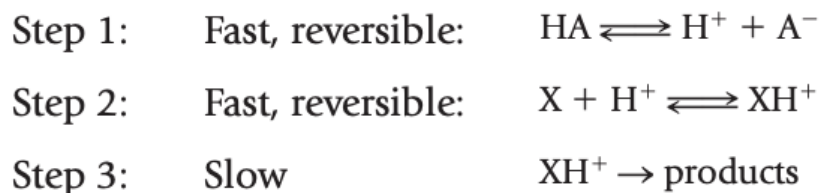
- Determine the rate law for this reaction

(b) One mechanism that has been proposed for this reaction is the following:



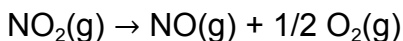
Show that the rate law predicted by this mechanism matches the experimentally determined rate law in part a.

92) Many biochemical reactions are catalyzed by acids. A typical mechanism consistent with the experimental results (in which HA is the acid and X is the reactant) is:



- a) What rate law is derived from this mechanism?
- b) What is the order of the reaction with respect to HA?
- c) How would doubling the concentration of HA affect the reaction?

85) The decomposition of nitrogen dioxide at a high temperature:



is second-order in this reactant.

(a) Determine the rate constant for this reaction if it takes 1.76 min for the concentration of  $\text{NO}_2$  to fall from 0.250 mol/L to 0.100 mol/L.

(b) If the chemical equation is written as:



what is the value of the rate constant?

84) The decomposition of  $\text{SO}_2\text{Cl}_2$  to  $\text{SO}_2$  and  $\text{Cl}_2$  is first-order in  $\text{SO}_2\text{Cl}_2$ .



$$\text{Rate} = k[\text{SO}_2\text{Cl}_2] \text{ where } k = 0.17/\text{h}$$

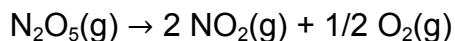
a) What is the rate of decomposition when  $[\text{SO}_2\text{Cl}_2] = 0.010 \text{ M}$ ?

b) What is the half-life of the reaction?

c) If the initial pressure of  $\text{SO}_2\text{Cl}_2$  in a flask is  $0.050 \text{ atm}$ , what is the pressure of all gases (i.e., the total pressure) in the flask after the reaction has proceeded for one half-life?

45) Calculate the activation energy,  $E_a$ , for the reaction  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  from the observed rate constants:  $k$  at  $25^\circ\text{C} = 3.46 \times 10^{-5} \text{ s}^{-1}$  and  $k$  at  $55^\circ\text{C} = 1.5 \times 10^{-3} \text{ s}^{-1}$

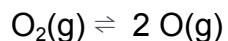
73) The decomposition of dinitrogen pentaoxide



has the following rate equation:  $\text{Rate} = k[\text{N}_2\text{O}_5]$ . It has been found experimentally that the decomposition is 20.5% complete in 13.0 hours at  $298 \text{ K}$ . Calculate the rate constant and the half-life at  $298 \text{ K}$ .

## Equilibrium

63) At 1800 K, oxygen dissociates very slightly into its atoms.



$$K_p = 1.2 \times 10^{-10}$$

If you place 0.050 mol of  $\text{O}_2$  in a 10.-L vessel and heat it to 1800 K, how many O atoms are present in the flask?

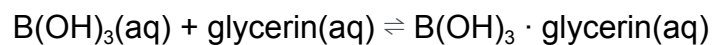
31) Dinitrogen trioxide decomposes to NO and  $\text{NO}_2$  in an endothermic process ( $\Delta_r H^\circ = 40.5 \text{ kJ/mol-rxn}$ ).



Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made.

- a) adding more  $\text{N}_2\text{O}_3(\text{g})$
- b) adding more  $\text{NO}_2(\text{g})$
- c) increasing the volume of the reaction flask
- d) lowering the temperature

65) Boric acid and glycerin form a complex



with an equilibrium constant of 0.90. If the concentration of boric acid is 0.10 M, how much glycerin should be added, per liter, so that 60.% of the boric acid is in the form of the complex?