CH353 – Physical Chemistry I
Spring 2012, Unique 52135

Exam 5
Friday, 27 April 2012

Name: Key

Useful Information:

$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 8.206 \times 10^{-2}\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

$1\ \text{atm} = 1.01325\ \text{bar} = 1.01325 \times 10^{5}\ \text{Pa} = 760\ \text{Torr}$

$0\ ^{\circ}\text{C} = 273.15\ \text{K}$

Always assume ideal gas unless directed otherwise.

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$
$$-\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$f(v)dv = 4\pi\left(\frac{FW}{2\pi RT}\right)^{3/2} v^2 \exp\left[\frac{-FWv^2}{2RT}\right]dv$$

Honor Code:
"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

_____
Signature Date

1. (24 points) True / False. Indicate whether the following statements are true or false.

a. True **False** The units of the rate constant *k* for a bimolecular reaction are mol L^{-1} s^{-1}.

b. **True** False The kinetic model of gases describes a system containing gas molecules that are in ceaseless random motion in all directions.

c. True **False** A catalyst is consumed as a reaction progresses.

d. True **False** The root-mean-square speed of a gas molecule is inversely proportional to the temperature of the system.

e. **True** False The Maxwell-Boltzmann distribution describes the probability of finding a gas particle moving a particular velocity *v*.

f. True **False** Unimolecular reactions are always first order in the reactant R.

g. **True** False Elementary reactions describe the mechanism by which reactions occur.

h. True **False** The steady-state approximation says that the concentration of an intermediate increases over time.

2. (20 points) Circle all of the following statements about reaction rate laws, *v(t)*, that are ALWAYS TRUE.

a. They are positive.

b. They can be determined from the stoichiometrically balanced equation.

c. The units of *v(t)* depend on the individual reaction.

d. Reaction orders are integer numbers.

3. (16 points) N_2O decomposes according to the following reaction:

$$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$$

At 900 K, the experimentally measured rate of this reaction is 6.2×10^{-6} mol L^{-1} s^{-1}. Determine the value of $d[N_2O]/dt$, $d[N_2]/dt$, and $d[O_2]/dt$.

$v(t) = 6.2 \times 10^{-6}$ mol/Ls

$d[N_2O]/dt = -2v(t) = -1.2 \times 10^{-5}$ mol/Ls

$\frac{d[N_2]}{dt} = 2v(t) = 1.2 \times 10^{-5}$ mol/Ls

$\frac{d[O_2]}{dt} = 6.2 \times 10^{-6}$ mol/Ls

4. (20 points) The mechanism for the decomposition of ozone is:

$$O_3 + Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + ClO$$

$$O_3 + ClO \xrightarrow{k_2} 2\,O_2 + Cl$$

Explain, in clear comprehensible English, the conditions that must be true for the steady-state approximation to apply to this mechanism.

The SSA implies that the intermediate, ClO·, is consumed as soon as it is formed. For this to be true, when ClO· is formed either the backwards rxn V_{-1} must be very fast, so $k_{-1} \gg k_1, k_2$, or the forwards rxn V_2 must be very fast, so $k_2 \gg k_{-1}, k_1$. Either of these conditions will allow the SSA to be true.

5. (20 points) Determine the frequency of collisions of nitrogen molecules with other nitrogen molecules in one cubic meter of air at 1 atm and 25°C. You may assume that air is 80% nitrogen and that the diameter of the nitrogen molecule is 3.8 Å.

$Z_{coll} = \dfrac{\sigma C_{rel} P}{k_B T}$

$P(N_2) = 0.8\ atm = 8.1\times10^4\ Pa$

$\sigma = \pi d^2 = \pi(3.8\times10^{-10}\ m)^2 = 4.5\times10^{-19}\ m^2$

$T = 298\ K$

$Fw(N_2) = 0.028\ kg/mol$

$C_{rel} = \sqrt{2}\,c = \sqrt{2}\left(\dfrac{3RT}{Fw}\right)^{1/2} = \sqrt{2}\left(\dfrac{3(8.314\ J/K\,mol)(298\ K)}{(0.028\ kg/mol)}\right)^{1/2} = 729\left(\dfrac{J}{kg}\right)^{1/2} = 729\ \dfrac{m}{s}$

$$Z_{coll} = \frac{(4.5\times10^{-19}\ m^2)(729\ m/s)(8.1\times10^4\ Pa)}{(1.38\times10^{-23}\ J/K)(298\ K)} = 6.5\times10^9\ \frac{Pa\,m^3}{s\,J} = \boxed{6.5\times10^9\ s^{-1} = Z_{coll}}$$