Name ___________________________ Test 2
PHYS 0111 (Gen Chem II) Spring 2005

A few equations:

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

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

$$t_{1/2} = [A]_0/(2\boldsymbol{k})$$

$$t_{1/2} = \frac{1}{\boldsymbol{k}[A]_0}$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{conc}_1]^x}{[\text{conc}_2]^x}$$

Integral Rate Laws

$$\ln[A]_t = -\boldsymbol{k}t + \ln[A]_0$$

$$1/[A]_t = \boldsymbol{k}t + 1/[A]_0$$

$$[A]_t = -\boldsymbol{k}t + [A]_0$$

Differential Rate Laws (general form)

$$\text{rate} = k[A]^x[B]^y$$

1. _______

2. _______

3. _______

4. _______

5. _______

6. _______

1. (5 pts. ea.) Write the equilibrium expression, K, for the following reactions.

a.

$2\ NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$ $\qquad K = [CO_2][H_2O]$

b.

$(CH_3)_3CCl(g) \rightleftharpoons (CH_3)_2CCH_2\ (g) + HCl(g)$ $\qquad K = \frac{[HCl][(CH_3)_2CCH_2]}{[(CH_3)_3CCl]}$

c.

$C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$ $\qquad K = \frac{[CO]^2}{[CO_2]}$

2. Rate and concentration data were collected for the following reaction.

$$2\ NO(g) + 2\ H_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$$

Experiment	Initial [NO]	Initial $[H_2]$	Initial –d[NO]/dt (M/s)
1	0.24	0.10	14.4×10^{-6}
2	0.12	0.10	3.6×10^{-6}
3	0.12	0.15	5.4×10^{-6}

a. (3 pts.) For experiment 1, determine the rate at which N_2 is being produced.

$$d[NO]/dt = \tfrac{1}{2}\,(-d[NO]/dt)$$

$$d[NO]/dt = \tfrac{1}{2}\,(14.4 \times 10^{-6}) = 7.2 \times 10^{-6}\ M/s$$

b. (10 pts.) Determine the differential rate law for the reaction. Do not determine the rate constant.

For NO

$\frac{14.4}{3.6} = \frac{(0.24)^x}{(0.12)^x}$

$4 = 2^x$

$x = 2$

For H_2

$\frac{5.4}{3.6} = \frac{(0.15)^y}{(0.10)^y}$

$1.5 = 1.5^y$

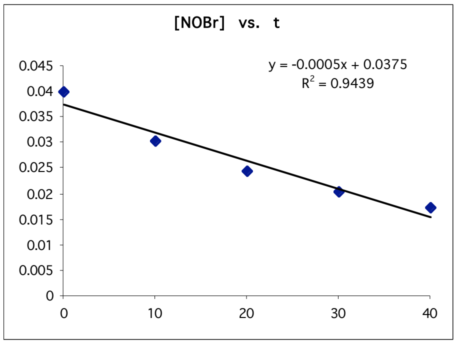
$y = 1$

rate = $k[NO]^2[H_2]$

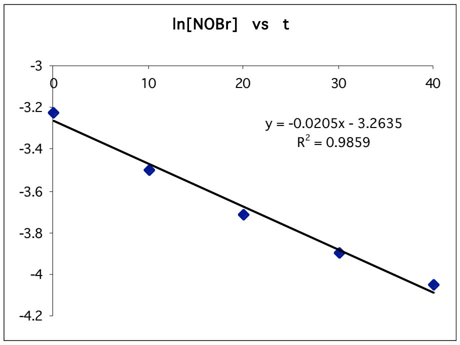
3. The concentration of NOBr was measured as the following reaction proceeded, and the data is tabulated below.

$$2\ NOBr(g) \longrightarrow 2\ NO(g) + Br_2(g)$$

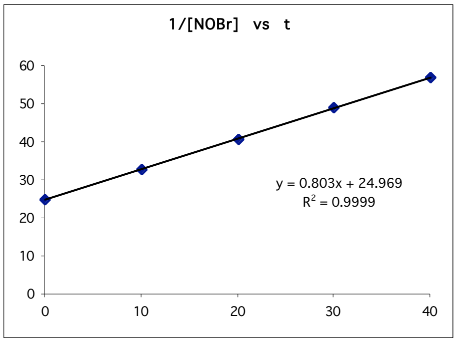
Time (s)	0	10	20	30	40
[NOBr]	0.0400	0.0303	0.0244	0.0204	0.0175



$y = -0.0005x + 0.0375$
$R^2 = 0.9439$



$y = -0.0205x - 3.2635$
$R^2 = 0.9859$



$y = 0.803x + 24.969$
$R^2 = 0.9999$

a. (6 pts.) What is the order of the reaction with respect to NOBr concentration?

The plot of 1/[NOBr] has the best correlation coefficient; therefore, the reaction is 2nd order with respect to NOBr concentration.

b. (4 pts.) How long does it take for the NOBr concentration to reach 0.0105 M?

$1/(0.0105) = 0.803\ t + 24.969$

$t = 87.5082123$ or $87.5\ s$

c. (4 pts.) Determine the differential rate law. Include the value for the rate constant with the appropriate units.

Since the order of the reaction was determined in part a, we know that the exponent for the differential rate law must be 2.

$\text{rate} = 0.803\ M^{-1} \cdot s^{-1}\ [NOBr]^2$

4. In tetrahydrofuran (THF), an organic solvent, $Mo(CO)_6$ reacts with $P(CH_3)_3$ to form $Mo(CO)_5(P(CH_3)_3)$. Experiments reveal that the rate of the reaction is 0 order with respect to the $P(CH_3)_3$ concentration and is 1st order with respect to $Mo(CO)_6$ concentration.

$$Mo(CO)_6 + P(CH_3)_3 \xrightarrow{\text{THF}} Mo(CO)_5(P(CH_3)_3) + CO$$

Two mechanisms have been proposed for the reaction.

Mechanism I

$$Mo(CO)_6 + P(CH_3)_3 \longrightarrow Mo(CO)_5(P(CH_3)_3) + CO$$

Mechanism II

$$Mo(CO)_6 \longrightarrow Mo(CO)_5 + CO \qquad \text{slow}$$

$$Mo(CO)_5 + P(CH_3)_3 \longrightarrow Mo(CO)_5(P(CH_3)_3) \qquad \text{fast}$$

a. (3 pts) Write the experimental rate law.

rate = k $[Mo(CO)_6]$ first order w/r/t $[MO(CO)_6]$ and zero order w/r/t $[P(CH_3)_3]$

b. (4 pts.) Determine the rate law predicted by mechanism I .

rate = k $[MO(CO)_6][P(CH_3)_3]$

c. (4 pts.) Determine the rate law predicted by mechanism II.

since step 1 is the slow step, the rate law is

rate = k $[MO(CO)_6]$

d. (3 pts.) Which mechanism is incorrect?

Mechanism 1 is incorrect because is predicts a rate law that doesn't match the experimental rate law.

5. (2 pts ea.) Identify whether each of the following statements about a dynamic equilibrium is true or false.

__TRUE__ At equilibrium, the concentrations of the reactants and the products do not change.

__TRUE__ At equilibrium, the rate at which the reactants are converted to products is the same as the rate at which products are converted to reactants.

__FALSE__ At equilibrium, the rate constant for the forward reaction is always equal to the rate constant for the reverse reaction.

__FALSE__ At equilibrium, the forward and reverse reactions stop.

__FALSE__ A large equilibrium constant means that when equilibrium is reached there will be more reactants than products present.

__TRUE__ A small equilibrium constant means that when equilibrium is reached there will be more reactants than products present.

6. (2 pts. ea.) The following statements refer to the relationship between a reaction's activation energy, E_a, the rate constant for the reactions, *k*, and temperature, T. Identify whether each statement is true or false.

__TRUE__ In general, reactions with large activation energies are slow.

__TRUE__ A reaction with a large rate constant is an intrinsically fast reaction.

__TRUE__ Typically, reactions with large rate constants have small activation energies.

__TRUE__ In general, as the temperature of a reaction is increased, the rate of the reaction is increased.

__FALSE__ As the temperature of a reaction is increased, the activation energy barrier is lowered.

__TRUE__ As the temperature of a reaction is increased, more reactant molecules are capable of overcoming the activation energy barrier.

__TRUE__ In general, increasing the temperature of a reaction increases the reaction's rate constant.