

Read questions carefully before answering. No outside paper is allowed. Use the reverse side of your answer paper as scratch. Use the periodic table and important constants charts provided.

(Total points = 42 + 42 + 16 = 100).

MULTIPLE CHOICE. Select the one alternative that best completes the statement or answers the question (3 pts each, if not mentioned otherwise).

1) Nitrogen dioxide decomposes to nitric oxide and oxygen via the reaction:

1) B? C



time (s)
0
100

M
0.0100
0.00650

$$\frac{(0.00650 - 0.0100) \text{ M}}{(100 - 0) \text{ s}} = -3.5 \times 10^{-5} \frac{\text{M}}{\text{s}}$$

$$= -3.5 \times 10^{-5} \frac{\text{M}}{\text{s}}$$

In a particular experiment at 300°C, $[\text{NO}_2]$ drops from 0.0100 to 0.00650 M in 100 s. The rate of disappearance of NO_2 for this period is _____ M/s. (4 pts.)

$$= -1.75 \times 10^{-5} \frac{\text{M}}{\text{s}}$$

A) 0.35

B) 1.8×10^{-3}

C) 3.5×10^{-5}

D) 7.0×10^{-3}

E) 3.5×10^{-3}

2) At elevated temperatures, dinitrogen pentoxide decomposes to nitrogen dioxide and oxygen: 2) A



$$\text{rate} = 2.2 \times 10^{-4} \frac{\text{M}}{\text{s}} = \frac{1}{2} \frac{[\text{N}_2\text{O}_5] \text{ M}}{\text{s}}$$

When the rate of formation of O_2 is 2.2×10^{-4} M/s, the rate of decomposition of N_2O_5 is

_____ M/s. (6 pts.)

A) 4.4×10^{-4}

B) 5.5×10^{-4}

C) 2.2×10^{-4}

D) 1.1×10^{-4}

E) 2.8×10^{-4}

The data in the table below were obtained for the reaction:



Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.273	0.763	2.83
2	0.273	1.526	2.83
3	0.819	0.763	25.47

$$\frac{2 \cdot k[A] (1.526)^n}{k[A] (0.763)^n} = \frac{2.83}{2.83}$$

$$\text{rate} = k[A]^2$$

$$k = \frac{\text{rate}}{[A]^2} = \frac{2.83}{(0.273)^2} = 37.97 \text{ M}^{-1} \text{ s}^{-1}$$

3) The rate law for this reaction is rate = _____. (4 pts.)

3) C

A) $k[A]^2[B]$

B) $k[A]^2[B]^2$

C) $k[A]^2$

D) $k[A][B]$

E) $k[P]$

4) The magnitude of the rate constant is _____. (6 pts.)

4) B

A) 2.21

B) 38.0

C) 13.2

D) 42.0

E) 0.278

5) Under constant conditions, the half-life of a first-order reaction _____.

5) E

A) is constant

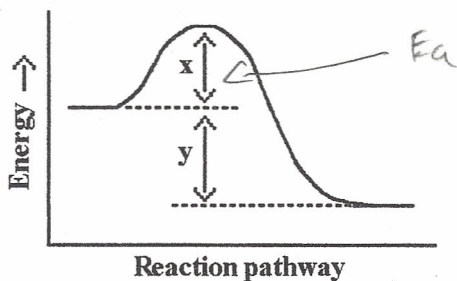
B) is the time necessary for the reactant concentration to drop to half its original value

C) can be calculated from the reaction rate constant

D) does not depend on the initial reactant concentration

E) All of the above are correct.

- 6) Which energy difference in the energy profile below corresponds to the activation energy for the forward reaction? 6) A



A) x

B) y

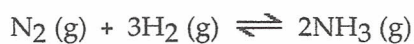
C) y - x

D) x - y

E) x + y

reverse!
↑

- 7) The equilibrium constant for the gas phase reaction



is $K_{\text{eq}} = 4.34 \times 10^{-3}$ at 300°C . At equilibrium, _____.

A) only products are present

B) products predominate

C) only reactants are present

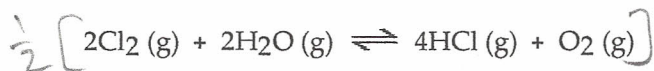
D) reactants predominate

E) roughly equal amounts of products and reactants are present

\lll reactants favored.

- 7) D

- 8) The K_{eq} for the equilibrium below is 7.52×10^{-2} at 480.0°C .



What is the value of K_{eq} at this temperature for the following reaction? (4 pts.)



$$= [K_{\text{eq}}]^{\frac{1}{2}} = (7.52 \times 10^{-2})^{\frac{1}{2}} = 0.274$$

A) 0.0752

B) 5.66×10^{-3}

C) 0.274

D) 0.150

E) 0.0376

- 9) Which of the following statements is true?

~~A) Q does not depend on the concentrations or partial pressures of reaction components.~~

~~B) Q does not change with temperature.~~

~~C) K_{eq} does not change with temperature, whereas Q is temperature dependent.~~

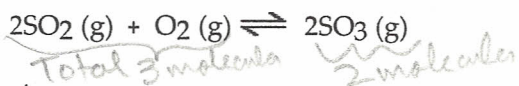
~~D) K does not depend on the concentrations or partial pressures of reaction components.~~

E) Q is the same as K_{eq} when a reaction is at equilibrium.

- 9) E

10) The reaction below is exothermic:

10) C



Le Chatelier's Principle predicts that _____ will result in an increase in the number of moles of $\text{SO}_3(\text{g})$ in the reaction container.

- A) removing some oxygen
- B) decreasing the pressure
- C) increasing the pressure
- D) increasing the temperature
- E) increasing the volume of the container

11) The effect of a catalyst on an equilibrium is to _____.

11) E

- A) shift the equilibrium to the right
- B) increase the rate of the forward reaction only
- C) slow the reverse reaction only
- D) increase the equilibrium constant so that products are favored
- E) increase the rate at which equilibrium is achieved without changing the composition of the equilibrium mixture

You will lose points if you dont show the (1) set up equation, (2) the raw data in the equation and (3) the appropriate units in your calculations.

12) If the rate of formation of oxygen gas is $6.0 \times 10^{-5} \text{ M/s}$ in the following conversion:

12) _____

$2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2$, then show your calculation to determine the rate of disappearance of $\text{O}_3(\text{g})$ at that instance (4 pts.).

$$\begin{aligned} \text{Rate} &= -\frac{1}{2} \frac{\Delta(\text{O}_3)}{\Delta t} = \frac{1}{3} \frac{\Delta(\text{O}_2)}{\Delta t} \\ \text{or } -\frac{\Delta(\text{O}_3)}{\Delta t} &= \frac{2}{3} \frac{\Delta(\text{O}_2)}{\Delta t} \\ &= \frac{2}{3} \cdot (6 \times 10^{-5} \frac{\text{M}}{\text{s}}) \\ &= 4 \times 10^{-5} \frac{\text{M}}{\text{s}} \end{aligned}$$

It fits well with the stoichiometry that less (2) number of O_3 molecules disappear for more (3) numbers of O_2 molecules, telling that O_3 disappears at a slower rate than oxygen appearance.

- 13) The initial rate of the reaction $A + B \rightarrow C$ was measured at several different concentrations of the reactants. Following formal methods,
 (a) calculate the rate law for the reaction (6 pts.) and
 (b) The magnitude of the rate constant (4 pts.).

13) rate = 0.4[A]²

Experiment	Initial Concentrations		Initial Rate (M s ⁻¹)
	[A] (M)	[B] (M)	
1	0.010	0.10	4.0 x 10 ⁻⁵
2	0.010	0.20	4.0 x 10 ⁻⁵
3	0.020	0.10	16.0 x 10 ⁻⁵

$$\text{rate} = k[A]^m[B]^n$$

$$\text{rate} = k[A]^2$$

$$k = \frac{\text{rate}}{[A]^2} = \frac{4.0 \times 10^{-5}}{(0.010)^2}$$

$$= 0.4$$

RATE LAW: rate = 0.4[A]²

second-order reaction overall.
 second order for A, zero order for B.

rate constant = k = 0.4

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[0.010]^m [0.20]^n}{k[0.010]^m [0.10]^n} = \frac{4.0 \times 10^{-5}}{4.0 \times 10^{-5}} = 1$$

$$2^n = 1$$

$$n = 0$$

$$(n \log 2 = \log 1)$$

$$n = \frac{\log 1}{\log 2} = 0$$

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[0.020]^m [0.10]^n}{k[0.010]^m [0.10]^n} = \frac{16.0 \times 10^{-5}}{4.0 \times 10^{-5}}$$

$$2^m = 4 \therefore m = 2$$

- 14) The rearrangement of methyl isonitrile to methyl nitrile has a rate constant of $5.25 \times 10^{-5} \text{ s}^{-1}$ at 198.9°C and $3.16 \times 10^{-3} \text{ s}^{-1}$ at 251.2°C . Calculate the energy of activation (E_a) of the reaction (8 pts.).

14) 161 kJ

$$k_1 = 5.25 \times 10^{-5} \text{ s}^{-1} \text{ (first order)}$$

$$T_1 = 198.9^\circ\text{C} + 273.15 = 472.05 \text{ K}$$

$$k_2 = 3.16 \times 10^{-3} \text{ s}^{-1}$$

$$T_2 = 251.2^\circ\text{C} + 273.15 = 524.35 \text{ K}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{E_a}{R} = \frac{\ln \frac{k_1}{k_2}}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$E_a = R \frac{\ln \frac{k_1}{k_2}}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)} = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \frac{\ln \frac{5.25 \times 10^{-5}}{3.16 \times 10^{-3}}}{\left(\frac{1}{524.35} - \frac{1}{472.05} \right)} = \frac{(8.314)(-4.0975)}{-2.113 \times 10^{-4}}$$

$$= 161227.109 \text{ J}$$

$$= 161.227109 \text{ kJ}$$

15) In the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$, if the $K_c = 9.60$ at 573 K, then calculate the K_p at this temperature. (6 pts.)

15) 4.34×10^{-3}

$$K_p = K_c (RT)^{\Delta n}$$

$\Delta n = \# \text{ moles products} - \# \text{ moles reactants}$

$$= 2 - (1 + 3) = -2$$

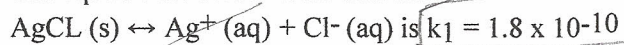
$$R = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

$$T = 573 \text{ K}$$

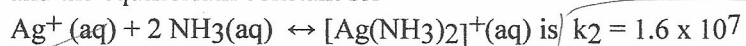
$$K_p = (9.60) \left[\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (573 \text{ K}) \right]^{-2}$$

$$= 0.0043378614 = 4.34 \times 10^{-3}$$

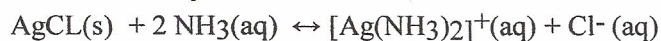
16) The equilibrium constant for reaction:



and the equilibrium constant for



Calculate the equilibrium constant, K_{net} for the net reaction (6 pts.):



K_c for net rxn = product of K_c s of individual steps.

thus $K_{\text{net}} = k_1 \cdot k_2 = (1.8 \times 10^{-10})(1.6 \times 10^7)$

$$= 0.00288 = 2.88 \times 10^{-3}$$

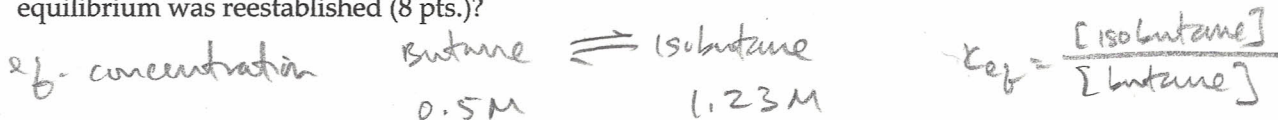
16) 2.9×10^{-3}

assuming 1:1 molar ratio.

$$[\text{Butane}]_b = 0.923 \text{ M}$$

$$[\text{Isobutane}]_{2g} = 2.31 \text{ M}$$

- 17) In the equilibrium rxn. Butane (g) \leftrightarrow Isobutane (g), assume equilibrium has reached in a 1.0 L flask with [Butane] = 0.5 M and [Isobutane] = 1.23 M at 298 K. The equilibrium constant for the reaction = 2.5 and afterwards 1.5 mol of Butane was added to the mixture. Calculate the new values of [Butane] and [Isobutane] when equilibrium was reestablished (8 pts.)?

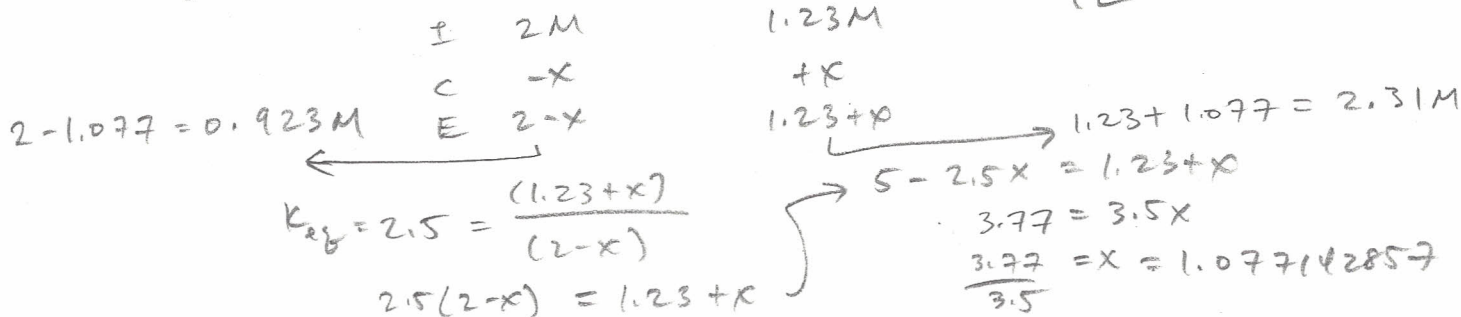


$$T = 298 \text{ K}$$

$$V = 1.0 \text{ L}$$

$$K_{eq} = 2.5$$

initial butane: $\frac{0.5 \text{ moles}}{1.0 \text{ L}} \times 1.0 \text{ L} = 0.5 \text{ moles}$
 $+ 1.5 \text{ moles}$
 $\frac{2 \text{ moles}}{1 \text{ L}} = 2 \text{ M}$



Answer if the statement is true or false (2 pts.) and then briefly explain your reasoning (2 pts.).

- 18) Rates of reaction can be positive or negative.

$$\text{rate} = k[A]^m[B]^n$$

However - rate of disappearance of reactants is negative, as we lose reactants for products.

the rate is dependent on reactant concentrations, reactant order, and rate constant, which is not negative - so the rate of a reaction is not negative (or else the rxn doesn't happen.)

T or F

- 19) Units of the rate constant of a reaction are independent of the overall reaction order.

we know that the rate constant units can be s^{-1} , $M^{-1}s^{-1}$, or $M^{-2}s^{-1}$ for zero, first, and second-order reactions (so that the rate has units $\frac{M}{s}$)

T or F

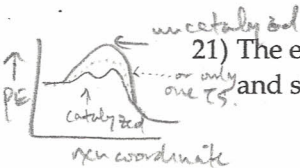
- 20) In an exothermic equilibrium reaction, increasing the reaction temperature favors the formation of reactants.



increasing temp/heat forces reaction to the left to "get rid of" the extra heat.

T or F

- 21) The effect of a catalyst on a chemical reaction is to react with product, effectively removing it and shifting the equilibrium to the right.



(Does not affect equilibrium concentration)

T or F

A catalyst changes the reaction mechanism, thereby facilitating the reaction (collisions between reactants with correct orientation) by improving orientation between the reactants (or products!) and reducing the activation energy of the reaction, speeding up the rate of reaction but not affecting the resulting equilibrium concentrations, which remain the same (K_{eq} is unaffected).

[see question 11]

Extra point question:

You will lose points if you don't show the (1) set up equation, (2) the raw data in the equation and (3) the appropriate units in your calculations.

- 22) Exactly 3.5 moles of N_2O_4 is placed in an empty 2.0-L container and allowed to reach equilibrium described by the equation 22) 0.58



If at equilibrium the N_2O_4 is 25% dissociated, what is the value of the equilibrium constant for the reaction (5 pts.)?

3.5 x .25 = 0.875

so 3.5 - 0.875 = 2.625 moles
(75% left)

$\frac{2.625 \text{ moles}}{2.0 \text{ L}} = 1.3125 \text{ M}$

		$N_2O_4(g)$	\rightleftharpoons	$2NO_2(g)$
I		$\frac{3.5 \text{ moles}}{2.0 \text{ L}} = 1.75 \text{ M}$		0
C		$x = 1.75 - 1.3125$ $= 0.4375 \text{ M}$		+2x
E		1.3125 M		$2x = 2(0.4375) = 0.875 \text{ M}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.875)^2}{(1.3125)} = 0.583333$$
$$= 0.583$$