Note that questions 1 to 4 were from an old unit, and should have been deleted!!!

5. What are the units for the rate constant of a third order reaction?

A) s-1 B) M-4s-1 C) M-2s-1 D) M-3s-1

6. For the reaction 2 A + 3 B ⭢ C, [A] is found to decrease at a rate of 1.0 M/s. If the rate law is rate = k[A], how fast does B decrease under the same conditions? A) 0.66 M/s B) 1.3 M/s C) 1.5 M/s D) 3.0 M/s

7. For the exothermic reaction 4 NH3(g) + 7 O2(g) ⭢4 NO2(g) + 6 H2O(g)

which change will increase the quantity of NO2 in an equilibrium mixture?

A) increasing temperature B) decreasing container volume

C) adding Ne (g) D) adding H2O(g)

8. Which accounts for the increase in the rate of a reaction when a catalyst is added to a chemical system? A) A decrease in the enthalpy change of the reaction B) an increase in the potential energy of the reactants

C) a decrease in the potential energy of the activated complex

D) a decrease in the entropy of the activated complex.

9. For this first order reaction CH3NC ⭢CH3CN, how do the properties of the reaction in the table below vary as the reaction proceeds at constant temperature?

|  |  |  |
| --- | --- | --- |
|  | Rate of reaction, -Δ[CH3NC]/Δt in M/s | Half life (s) |
| A) | remains the same | decreases |
| B) | decreases | remains the same |
| C) | remains the same | remains the same |
| D) | decreases | decreases |

10. A reaction was found to be third order in carbon monoxide concentration. How does the rate of the reaction change if the [CO] is tripled, with everything else kept the same? The rate A) triples B) remains unchanged C) increases by a factor of 27

D) increases by a factor of 9

11. The rate of a reaction between A and B follows the rate law Rate = k[A]2[B]

Determine the rate of Experiment Two in the table below. Both experiments occur at the same temperature.

|  |  |  |  |
| --- | --- | --- | --- |
| Experiment | [A] | [B] | Rate, in M/s |
| 1 | 0.10 | 0.10 | R |
| 2 | 0.20 | 0.30 | ? |

A) 3 R B) 6 R C) 12 R D) 18 R

12. C(s) + H2O(g) ⇄ CO(g) + H2(g). ΔH > 0.

For the system above, which changes will increase the amount of H2(g) at equilibrium?

I. Adding C(s)

II. Increasing the volume of the container

III. Increasing the temperature

A) I only B) III only C) II and III only D) I, II, and III

13.What quantity is represented by the absolute value of the slope of the dashed line in the accompanying diagram for the concentration change in a reaction against time?

A) instantaneous rate of reaction B) rate constant C) reaction order

D) activation energy

14. Which statement is true about a reactant that appears in the balanced equation of a reaction but does not appear in the rate equation?

A) It is an inhibitor B) It is not part of the reaction C) Its concentration is too low to be significant D) It takes part in the reaction after the rate determining step

15. 2 NO(g) + O2 (g) ⇄ 2 NO2(g) ΔH < 0

The effect of a temperature increase on this reaction is that it would

A) increase both the equilibrium constant and the rate constant

B) decrease both the equilibrium constant and the rate constant

C) increase the rate constant while decreasing the equilibrium constant

D) decrease the rate constant while increasing the equilibrium constant

16. 2 SO2(g) + O2(g) ⭢ 2 SO3(g). When 2.00 mol of O2 and 2.00 mol. of SO2 are placed in a 1.00 liter container and allowed to come to equilibrium at a certain temperature, the mixture is found to contain 1.00 mole of SO3(g). What is the value of the Kc at that temperature?

A) 1.00 B) 0.33 C) 0.67 D) 3.0

17 - 21 refer to the following: PCl5(g) ⭢ PCl3(g) + Cl2(g)

PCl5(g) decomposes into PCl3(g) and Cl2(g) according to the equation above. A pure sample of PCl5(g) is placed in a rigid, empty 1.00 liter container. The initial pressure of the PCl5 is 1.00 atm. The temperature is held constant until equilibrium is reached. At equilibrium, the TOTAL pressure in the container is 1.40 atm.

17. Which is the most likely cause of the increase in pressure that is observed as the reaction reaches equilibrium? A) a decrease in the strength of the intermolecular attractions between the molecules B) an increase in the strength of the intermolecular attractions C) an increase in the number of molecules, leading to increased collisions with the container walls D) an increase in the speed of the molecules that increased both the number and intensity of collisions with the container walls.

18. As the reaction moves toward equilibrium, the rate of the forward reaction

A) increases until it equals the rate of the reverse reaction

B) remains constant because the temperature is constant

C) decreases but never reaches zero D) decreases until it reaches zero

19. If the reaction were to go to completion, the total final pressure in the container would be A) 1.4 atm. B) 2.0 atm. C) 2.8 atm. D) 3.0 atm.

20. Based on the initial and equilibrium pressures, the Kp of this reaction is

A) 1 B) greater than 0.1 but less than 1 C) greater than 1 but less than 2

D) greater than 2

21. Additional Cl2(g) is added to the equilibrium system. Which best describes the changes in the rate of the **reverse** reaction that would occur?

A) The rate would first increase, but then decrease until it reached the same rate it showed in the initial equilibrium system

B) The rate would first increase, but then decrease until a new equilibrium was reached, in which the reverse rate was greater than in the initial system.

C) The rate would first increase, but then decrease to reach a new equilibrium in which the reverse rate was slower than in the initial system

D) The rate would increase steadily until a new equilibrium was reached.

22 to 23 are based on the gas phase reaction 2 N2O5 ⭢ 4 NO2 + O2

A sample of N2O5 (g) is placed in an evacuated container, and the reaction above occurs. The value of the PN2O5 , the partial pressure of N2O5, was measured during the reaction and recorded in the table below.

|  |  |  |  |
| --- | --- | --- | --- |
| Time in minutes | P N2O5 in atm. | Ln( P N2O5) | 1  P N2O5 |
| 0 | 150 | 5.0 | 0.0067 |
| 100 | 75 | 4.3 | 0.013 |
| 200 | 38 | 3.6 | 0.027 |
| 300 | 19 | 2.9 | 0.053 |

22. Based on this data, the decomposition of N2O5 is a

A) zero order reaction B) first order reaction C) second order reaction

D) third order reaction.

23. The value of the rate constant is A) 0 .070 min-1 B) 0.0070 min-1

C) 100. atm-1/min D) 6.3 x 10-5 atm-1/min

The data in the table below were obtained for the reaction A + B ª P

|  |  |  |  |
| --- | --- | --- | --- |
| Run number | initial [A] M | initial [B] M | Initial rate, M/s |
| 1  2  3 | 0.273  0.273  0.819 | 0.763  1.526  0.763 | 2.83  2.83  25.47 |

24. The rate order of the reaction in A is A) first B) second C) third D) zero

25. The order of the reaction in B is is A) first B) second C) third D) zero

26. What is the numerical value of the rate constant?

A) 13.6 B) 49.8 C) 38.0 D) 4.86 E) 57.0

28. At high temperatures, (NH4)2CO3 decomposes as follows:

(NH4)2CO3(s) ⇄ 2 NH3(g) + CO2(g) + H2O (g)

Solid ammonium carbonate is added to a container, and at a certain temperature, the partial pressure of NH3(g) is determined to be 4.00 atm at equilibrium. What is the value of the Kp for the reaction at that temperature?

A) 64.0 B) 16.0 C) 256 D) 4.00 E) 128

Questions 29 and 30 are based on the graph below for the chemical reaction below:

lnvstime

29. Based on this graph, we would assume that the overall reaction is

A) first order B) second order C) third order D) zero order

30 . The slope of this line is equal to ( where "k" is the rate constant)

A) k B) -k C) 1/k D) Ln k

31-32 : 2 SO3(g) ⇄ 2 SO2(g) + O2(g) ΔH° = + 200 kJ

31. After equilibrium is established in this reaction, some pure O2(g) is injected into the reaction vessel at constant temperature. Once equilibrium has been reestablished, which of the following has a **lower** value compared to its value in the original equilibrium?

A) Keq for the reaction B) The total pressure in the reaction vessel.

C) The amount of SO3(g) in the reaction vessel.

D) The amount of SO2(g) in the reaction vessel.

32. Which set of changes would produce the greatest **increase** in the quantity of SO3 in the reaction vessel? A) increase the temperature, and increase the size of the vessel B) decrease the temperature and decrease the size of the vessel C) increase temperature and decrease the size of the vessel D) decrease temperature and increase the size of the vessel

33. H2(g) + I2(g) ⇄ 2 HI (g) Kc = 36 at a certain temperature.

A mixture of 1.00 mole of Hydrogen gas and 1.00 mole of iodine gas is placed in a 1.00 liter flask at constant temperature, and allowed to reach equilibrium. Based on the given Kc, what is the molar concentration of H2 in the equilibrium mixture?

A) 0.500 M B) 1.00 M C) 0.75 M D) 0.25 M E) 1.25 M

34. Which of the following expressions is the correct equilibrium constant expression for the following reaction? CO2 (g) + 2H2 (g) ⇄ CH3OH (g)

A)  B)  C)  D) 

(1) SO2 (g) + (1/2) O2 (g) ⇄ SO3 (g)

(2) 2SO3 (g) ⇄ 2SO2 (g) + O2 (g)

35. The equilibrium constant for reaction 1 is K. The equilibrium constant for reaction 2 is A) K2 B) 2K C) 1/2K D) 1/K2 E) -K2

36) At 900.0 K, the equilibrium constant (Kp) for the following reaction is 0.345.

2SO2 + O2 (g) ⇄ 2SO3 (g)

At equilibrium, the partial pressure of SO2 is 35.0 atm and that of O2 is 15.9 atm. The partial pressure of SO3 is \_\_\_\_\_\_\_\_\_\_ atm.

A) 82.0 B) 4.21 × 10-3 C) 192 D) 6.20 × 10-4 E) 40.2

PROBLEMS

I. Assume that the decomposition of H2O2  H2O2(*l*) → H2O (*l*) + ½ O2(g)

is first order. At a certain temperature, it is found that it takes 90.0 minutes for a 2.00 M solution of H2O2 to decompose to a conc. of 1.50 M.

A. What is the rate constant for the decomposition at that temperature? ( you need not change the time unit to seconds. Minutes are fine) 3.20 x 10-3 /min

B. Starting with a concentration of 1.50 molar, how long would it take until the concentration became 0.50 molar? 343 min.

C. What is the half life of the reaction, in minutes? 216

II Suppose that the peroxide decomposition can proceed by the following mechanism:

1. H2O2 (aq) + Br−(aq)→ H2O (l) + BrO−(aq)

2. BrO- (aq) → Br–  (aq) + ½ O2 (g)

A. In the mechanism above, identify an intermediate and a catalyst I = BrO-, c = Br-

B. Write the net reaction produced through the mechanism above.H2O2 → H2O + ½ O2

C. Write the rate law, if the first step shown above is the rate determining step.

Rate = k [ H2O2][[Br-]

III. Assume that the reaction 2 SO3(g) ⇄ 2 SO2(g) + O2(g) is **second**  order. The initial pressure of the SO3 gas is 2.00 atm. After 90.0 seconds, the pressure of the SO3 gas is 1.80 atm. What would the pressure of the SO3 gas be after 300. seconds?

(Not covered this term) k = 6.17 x 10-4 M-1/s 1/x - 1/ 2 = 6.17 x 10-4 )( 300 ) x = 1.46 atm.

IV. NH4HS*(s)* ⭢ NH3*(g)* + H2S*(g)* ΔHº = +93 kilojoules

The equilibrium above is established by placing solid NH4HS in an evacuated container at 25ºC. At equilibrium, some solid NH4HS remains in the container. Predict and explain each of the following.

(a) The effect on the equilibrium partial pressure of NH3 gas when additional solid NH4HS is introduced into the container. No effect. Solids do not shift equilibria

(b) The effect on the equilibrium partial pressure of NH3 gas when additional gaseous H2S is introduced into the container Decreases. The reaction shifts to form less produce.

(c) The effect on the mass of solid NH4HS present when the volume of the container is decreased . Increases. Decreased volume increases the pressure of both gases, which increases Q. Reaction shifts toward reactant.

(d) The effect on the mass of solid NH4HS present when the temperature is increased

Decreases. The forward, endothermic reaction is favored by inc T.

V. SO2Cl2(g) ⭢ SO2(g) + Cl2(g)

A 4.32 gram sample of SO2Cl2 is placed in a rigid, evacuated 1.50 L reaction vessel. As the container is heated to 400. K, the sample starts to decompose according to the equation above. The decomposition reaction is **endothermic.**

4.31g/ 135 g/mol = 0.032 mol. P = nRT/V = 0.032 x 0.0821 x 400/ 1.5 = 0.700 atm.

A. What is the pressure, in atm., of the SO2Cl2 (g) before any decomposition takes place?

B. When the system has reached equilibrium at 400. K the total pressure in the container is 1.26 atm. Calculate the partial pressures, in atm., of SO2Cl2, SO2, and Cl2 at equilibrium. .14, .56, .56

C. i Write the equilibrium expression for Kp for the reaction and

ii. calculate the value of the equilibrium constant, Kp. 2.24

D. The temperature of the equilibrium mixture is increased to 425 K. Will the value of Kp increase, decrease or remain the same? Justify your prediction.

It will increase because the reaction is endothermic.

E. In another experiment, the original partial pressures of SO2Cl2, SO2, and Cl2

are each 1.0 atm. at 400. K. Predict whether the amount of SO2Cl2 will increase, decrease or remain the same as the reaction comes back to equilibrium. Justify your prediction.

Kp at 400 K was found to be 2.24. If all the pressures are 1.0 atm, then Q = 1. Since

Q<K, the reaction will shift to form more product. SO2Cl2 will decrease.

VI. 2 A + B C + D.

The following results were obtained when the reaction above was studied at 25°C:

|  |  |  |  |
| --- | --- | --- | --- |
| Experiment | Initial [A] | Initial [B] | Initial Rate of  Formation of C  in mol L-1 min-1 |
| 1 | 0.25 | 0.75 | 4.3 x 10-4 |
| 2 | 0.75 | 0.75 | 1.3 x 10-3 |
| 3 | 1.50 | 1.50 | 5.2 x 10-3 |
| 4 | 1.75 | ? | 8.0 x 10-3 |
|  |  |  |  |

A. Determine the order of the reaction with respect to A and B. Justify your answer

A is first order, when it triples, the rate is 3x faster. B is 1st order. When A doubles between exp. 2 and 3, that will make the rate 2 x greater. But the rate IS 4x greater, which means that doubling B also doubled the rate.

B. Write the rate law for the reaction. Calculate the value of the rate constant, and include correct units.

Rate = k[A][B]. k = 2.3 x 10-3 M-1/min

C. Determine the initial rate of disappearance of A in experiemnt 3.

1.04 x 10-2 M/min

D. Determine the initial value of [B] in experiment 4 2.0 M

E. Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (B) Justify your choice.

1. A + B ⭢ C + M Fast

M + A ⭢D slow.

2. B ⇄ M Fast, equilibrium

M + A ⭢C + X slow

A + X ⭢D fast

3. A + B ⭢M Fast equilibrium

M + A ⭢C + X slow

X ⭢D fast

VII. C2H4(g) reacts with HCl(g) as follows:

C2H4(g) + HCl(g) ⭢ C2H5Cl (g) ΔH̊ = -72.6 kJ/molrxn

a) When HCl(g) is injected into the container of C2H4(g) at 450 K, the total pressure increases. Then, as the reaction proceeds at constant T, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level. The reaction decreases the number of gas particles, so the pressure dec.

Suppose that the reaction proceeds via the following two step mechanism.

Step 1: C2H4(g) + HCl(g) ⭢C2H5+(g) + Cl– (g) rate determining step

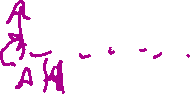
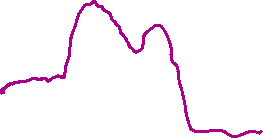
Step 2: C2H5+(g) + Cl– (g) ⭢C2H5Cl(g) fast step

b) Write the rate law for the reaction that is consistent with the mechanism above.

c) Identify an intermediate in the reaction mechanism above.

Rate = k[ C2H4][HCl] The intermediate is Cl- OR, C2H5-

d) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two step mechanism and the enthalpy change of the reaction.



E. On the diagram, clearly indicate the activation energy, Ea, for the rate determining step in the reaction.