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## Constants and Conversion Factors

$N_A = 6.02 \times 10^{23}$ mol$^{-1}$

$R = 8.31$ J/mol-K $= 8.31$ kPa-L/mol-K

1 bar = 100 kPa = 750 torr

1 kPa = 7.50 torr

1 J = 1 kPa-L

(129 pts) **PART I.  MULTIPLE CHOICE (Circle the ONE correct answer)**

1.  A sample of decane, $C_{10}H_{22}$ (M=142), contains $5.0 \times 10^{24}$ atoms of Hydrogen.  What is the mass of the sample?

    (A)  28.4 g          **(B)  53.6 g**          (C)  1180 g          (D)  $2.6 \times 10^4$ g

2.  The pressure of a sample of $O_2(g)$ is 350 torr in a 50 L container at 400 °C.  What is the pressure of this gas in a 20 L container at 100 °C?

    (A)  1580 torr          **(B)  485 torr**          (C)  220 torr          (D)  78 torr

3.  How many molecules of $CO_2$ (M=44) are contained in a 15 L container at 150 °C and 1.0 bar?

    (A)  $7.2 \times 10^{23}$          (B)  $2.6 \times 10^{21}$          (C)  $5.8 \times 10^{22}$          **(D)  $2.6 \times 10^{23}$**

4.  A sample of $C_4H_{10}(g)$ [M=58] effuses through a pinhole in 60. s.  An equivalent amount of an unknown gas, X, effuses through the pinhole in 90 s.  What is the approximate Molar Mass of the uinknown gas?

    (A)  26 g/mol          (B)  45 g/mol          **(C)  131 g/mol**          (D)  87 g/mol

5.  A 110 gram sample of $CO_2(g)$ (M=44) is initially at 75 °C.   When 5.0 kJ of heat is **removed** from the sample at constant pressure, the final temperature is 21 °C.  The constant pressure molar heat capacity of $CO_2$ is approximately:

    (A)  28.8 J/mol-K          (B)  51.7 J/mol-K          (C)  92.6 J/mol-K          **(D)  37.0 J/mol-K**

6.  When a gas is cooled at constant pressure, :

    **(A)  w > 0 , $\Delta H$ < 0**          (B)  w < 0 , $\Delta H$ < 0

    (C)  w < 0 , $\Delta H$ > 0          (D)  w = 0 , $\Delta H$ < 0

7.  What are q and $\Delta H$ when 2 moles of a gas is expanded reversibly and isothermally from 5 L to 40 L at 25 °C?

    (A)  q= -10.3 kJ, $\Delta H$= 0          **(B)  q= +10.3 kJ, $\Delta H$=0**

    (C)  q=0, $\Delta H$= 0          (D)  q=0, $\Delta H$=+10.3 kJ

8.  Zinc reacts with Hydrochloric acid according to the reaction:
    $Zn(s) + HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$.   What is the work, in kJ, when 1.5 moles of $Zn(s)$ react with an excess of $HCl(aq)$ at 1 bar and 30 °C?

    **(A)  -3.8 kJ**          (B)  -2.5 kJ          (C)  +3.8 kJ          (D)  +2.5 kJ

9.  What is the approximate work involved when 230 g of toluene, $C_7H_8$,(M=92) is vaporized at 1 bar and 111 °C (its normal boiling point)?

    (A)  +2.3 kJ          (B)  +87.9 kJ          **(C)  -8.0 kJ**          (D)  -2.3 kJ

10. The Enthalpy of Vaporization of toluene (M=92) is 38.1 kJ/mol. What iis the approximate value of the Internal Energy change, $\Delta U$, when 230 g of toluene, $C_7H_8$, is vaporized at 1 bar and 111 °C (its normal boiling point)?

(A) +87.3 kJ     (B) 95.3 kJ     (C) 103.2 kJ     (D) -95.3 kJ

11. The constant pressure molar heat capacity of $CO_2(g)$ is 37.1 J/mol-K. What is $\Delta S$ when 3 moles of $CO_2(g)$ is cooled at constant pressure from 200 °C to 50 °C?

(A) 9.5 J/K     (B) -154.3 J/K     (C) +154.3 J/K     (D) -42.5 J/K

12. A sample of 0.5 moles of $O_2(g)$ originally at 500 kPa and 5 L is expanded reversibly and isothermally to a final volume of 25 L. What is $\Delta S$ for this process?

(A) +4030 J/K     (B) +6.7 J/K     (C) +13.4 J/K     (D) -6.7 J/K

13. From the following thermochemical equations,

$$2\ H_2O(g) \rightarrow 2\ H_2(g) + O_2(g) \qquad \Delta H= +484\ kJ$$
$$2\ O_3(g) \rightarrow 3\ O_2(g) \qquad \Delta H= +286\ kJ$$
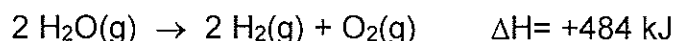
$\Delta H$ for the reaction, $3\ H_2O(g) \rightarrow 3\ H_2(g) + O_3(g)$, is

(A) +583 kJ     (B) +341 kJ     (C) -583 kJ     (D) -869 kJ

14. The reaction, A → B, is **endergonic** at 25 °C and the entropy change is +40 J/K. What can be concluded about the enthalpy change for this reaction?

(A) $\Delta H > +11.9$ kJ     (B) $\Delta H < -11.9$ kJ     (C) $\Delta H > 18.4$ kJ
(D) No conclusion can be made about $\Delta H$

15. For the **endergonic** reaction, C → D, $\Delta H = -30$ kJ. For this reaction,

(A) $\Delta G > 0$ and $\Delta S > 0$         (B) $\Delta G < 0$ and $\Delta S < 0$
(C) $\Delta G < 0$ and $\Delta S > 0$         (D) $\Delta G > 0$ and $\Delta S < 0$

16. The normal melting point of toluene is -95 °C. The enthalpy of fusion of toluene is 6.6 kJ/mol. What is the entropy change of the **system** when one mole of liquid toluene crystallizes to solid toluene at -95 °C?

(A) +69 J/mol-K     (B) -37 J/mol-K     (C) -69 J/mol-K     (D) +37 J/mol-K

17. The Enthalpy of Fusion of acetone is 5.7 kJ/mol. The Entropy of Fusion of Acetone is 32.0 J/mol-K. What is $\Delta G$ when 1 mole of liquid acetone is crystallized to the solid at 20 °C?

(A) -3.7 kJ     (B) 0 kJ     (C) +3.7 kJ     (D) -15.1 kJ

18. When 30 grams of glucose (M=180) is added to 70 grams of water, the density of the solution is 1.20 g/mL.  What is the Molarity of the solution?

(A)  1.4 M        (B)  1.7 M        (C)  2.0 M        (D)  2.4 M

19. When 42.4 grams of the strong electrolyte $K_3PO_4$ [M=212] is dissolved in 100 grams of water ($K_b$=0.5 °C/m), the boiling point of the solution is

(A)  96 °C        (B)  104 °C        (C)  101 °C        (D)  99 °C

20. The normal boiling point of pure $CCl_4$(l) is 77 °C and the boiling point elevation constant is 5.0 °C/m. When 5 grams of an unknown compound is placed in 100 grams of $CCl_4$, the boiling point of the solution is 84.5 °C.  The Molar Mass of the unknown compound is approximately:

(A)  33 g/mol        (B)  64 g/mol        (C)  128 g/mol        (D)  3.3 g/mol

21. When 10. grams of glucose (M=180) is dissolved in 200 mL of aqueous solution, the osmotic pressure at 100 °C is:

(A)  1.7 bar        (B)  860 bar        (C)  2.3 bar        (D)  8.6 bar

**For #22 - #26:**  Consider the gas phase equilibrium, $4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$. The enthalpy change for  this reaction is $\Delta H^0$ -340 kJ, and the equilibrium constant is K = 8 at 175 °C  ($\Delta G^0$ -7.74 kJ).

22. For the above reaction, if the volume of the container is **increased,**

(A)  the equilibrium will move to the left and K will decrease
(B)  the equilibrium will move to the right and K will increase
(C)  the equilibrium will move to the left and K will remain constant
(D)  the equilibrium will move to the right and K will remain constant

23. For the above reaction, if the temperature is **increased,**

(A)  the equilibrium will move to the left and K will decrease
(B)  the equilibrium will move to the right and K will increase
(C)  the equilibrium will move to the left and K will remain constant
(D)  the equilibrium will move to the right and K will remain constant

24. What is $\Delta G$ for this reaction at 175 °C when the pressures are:  P(NO_2) = 0.5 bar, P(O_2) = 0.3 bar and P(N_2O_5) = 2.0 bar?

(A)  -27.7 kJ        (B)  -7.7 kJ        (C)  +20.0 kJ        (D)  +12.2 kJ

25. What is the approximate value of the equilibrium constant, K, for the above reaction at 150 °C?

(A)  220        (B)  1770        (C)  $3.6 \times 10^{-2}$        (D)  $4.5 \times 10^{-3}$

26. What is K for the reaction, $N_2O_5 \rightleftharpoons 2NO_2(g) + \frac{1}{2}O_2(g)$ at 175 °C.

(A) 0.35   (B) 0.25   (C) 2.8   (D) 4.0

27. For the gas phase equilibrium, $2A(g) + B(g) \rightleftharpoons 2C(g)$, the equilibrium constant is

$K = 1 \times 10^{-3}$. If one puts A and B into a vessel with initial pressures, $P_{init}(A) = P_{init}(B) = 3$. bar, what is the pressure of C at equililbrium?

**NOTE:** You may assume that very little A and B react.

(A) 0.045 bar   (B) 0.164 bar   (C) 0.082 bar   (D) 0.063 bar

**For #28 - #29:** Hydrocyanic acid, HCN, is a weak acid with acid dissociation constant, $Ka = 5.0 \times 10^{-10}$.

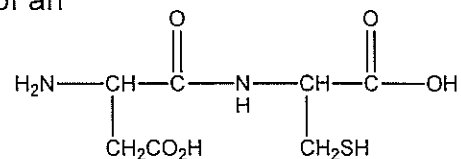28. What is the pH of 0.2 M potassium cyanide, KCN?
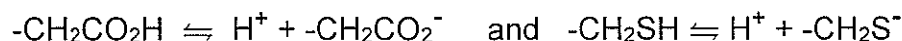
(A) 2.7   (B) 5.0   (C) 9.0   (D) 11.3

29. What is the pH of 2 Liters of 0.3 M KCN following the addition of 0.2 mol of HCl?

(A) 5.0   (B) 9.0   (C) 9.6   (D) 9.8

**For #30 - #33:** Consider the dipeptide (Pep) consisting of an Aspartic Acid residue and a Cysteine residue (pictured on right)

The two side groups ionize according to:

$-CH_2CO_2H \rightleftharpoons H^+ + -CH_2CO_2^-$   and   $-CH_2SH \rightleftharpoons H^+ + -CH_2S^-$



The four pKa's are: $pK_a'$ ($\alpha$-CO$_2$H) = 1.9, $pK_a''$ ($\beta$-CO$_2$H) = 3.9, $pK_a'''$(CH$_2$SH) = 8.5 and $pK_a''''$($\alpha$-NH$_3^+$) = 9.9

30. What is the pH after 2.0 equivalents of NaOH are added to a solution containing the most acidic form of Pep?

(A) 2.9   (B) 3.9   (C) 6.2   (D) 8.5

31. What pH corresponds to the isoelectric point, pI, of Pep?

(A) 2.9   (B) 3.9   (C) 6.2   (D) 9.2

32. What is the average charge of Pep at pH = 8.5?

(A) -1.5   (B) -0.5   (C) -2.0   (D) -2.5

33. What form of the peptide is present in highest concentration in a Pep solution buffered to pH = 5.0?

(A) $Pep^{1+}$      (B) Pep      (C) $Pep^{1-}$      (D) $Pep^{2-}$

34. The reaction, A → Products, is of order "x"; therefore, the initial rate, $r_o = k[A]_o^x$. When $[A]_o$= 0.2 M, $r_o$= 0.10 M/s. When $[A]_o$= 0.8 M, $r_o$= 6.40 M/s. Therefore, the reaction order, x, is

(A) 1.0      (B) 2.5      (C) 2.0      (D) 3.0

35. Consider a second order reaction, rate = $k[A]^2$, with a rate constant, k = 0.03 $M^{-1}s^{-1}$. If one starts with an initial concentration, $[A]_o$ = 0.80 M, approximately how long will it take for the concentration of A to decrease to 0.30 M?

(A) 70 s      (B) 140 s      (C) 35 s      (D) 320 s

36. Consider a zeroth order reaction, rate = $k[A]^0$= k, When the initial concentration of A is 0.70 M, the hallf life of the reaction is 5.0 s. What is the approximate value of the rate constant for this zeroth order reaction?

(A) 0.14 $Ms^{-1}$      (B) 0.07 $Ms^{-1}$      (C) 0.29 $Ms^{-1}$      (D) 0.035 $Ms^{-1}$

37. The reaction, $2NO + O_2 → 2NO_2$, proceeds by a two step mechanism:

(1) $2NO \rightleftharpoons N_2O_2$ (fast pre-equilibrium characterized by the equilibrium constant, K),

(2) $N_2O_2 + O_2 → 2NO_2$ (slow rate-determining step, characterized by the rate constant, k). The rate law for the formation of product is of the form:

(A) $k_{eff}[NO][O_2]$    (B) $k_{eff}[N_2O_2][O_2]^2$    (C) $k_{eff}[NO]^{1/2}[O_2]$    (D) $k_{eff}[NO]^2[O_2]$

**For #38 - #39:** Consider an enzyme catalyzed reaction for which the slope and intercept of the Lineweaver-Burk (double reciprocal) plot are: Slope= 0.02 s, Intercept= 0.01/mM s.

38 For this reaction, the maximum velocity, $V_m$, is

(A) 0.5 mM $s^{-1}$      (B) 100 mM $s^{-1}$      (C) 50 mM $s^{-1}$      (D) 2.0 mM $s^{-1}$

39. For this reaction, the Michaelis constant, $K_M$, is

(A) 0.002 mM      (B) 0.50 mM      (C) 2.0 mM      (D) 500 mM

40. For an enzyme catalyzed reaction, $V_m$= 50 mM/s and $[E]_o$= 0.05 mM. Therefore, the "turnover number", $k_2$, is

(A) 1000 $s^{-1}$      (B) 0.001 s      (C) 0.4 s/mM      (D) 2.5 mM/s

41. When an inhibitor is added to an enzyme catalyzed reaction, it is found that the intercept of the Lineweaver-Burk plot is increased, but the slope is not affected.. Therefore, the type of inhibition is

(A) Uncompetitive  (B) Noncompetitive  (C) Competitive  (D) Briggs-Haldane

**For #42 - #43:** Consider an enzyme catalyzed reaction with $K_M$= 40 mM, $V_m$= 150 $\mu$M/s, and [S]= 80 mM. An **Uncompetitive** inhibitor to this reaction has an inhibitor constant, $K_I$= 20 mM.

42. What is the initial velocity, $v_0$, in the absence of the inhibitor?

(A) 50 $\mu$M/s     (B) 120 $\mu$M/s     (C) 100 $\mu$M/s     (D) 225 $\mu$M/s

43. What is the percent inhibition (i%) when the inhibitor concentration is [I]= 50 mM?

(A) 38%          (B) 45%          (C) 71%          (D) 63%

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(30)     **PART II.   THREE (3) PROBLEMS FOLLOW (Show work for partial credit)**

(08)  1.   The reaction, 2 C + D → P (P is the product) proceeds by the following mechanism:

$$k_1 \qquad\qquad\qquad\qquad k_2$$
$$C + D \rightleftharpoons I \qquad \text{followed by} \quad I + C \rightarrow P$$
$$k_{-1}$$

"I" is an intermediate present in steady-state concentration. Use the steady-state approximation on [I] to develop an expression for the rate of formation of P as a function of [C], [D], $k_1$, $k_{-1}$ and $k_2$.

$$SS\ Approx \qquad \frac{d[I]}{dt} = 0 = k_1[C][D] - k_{-1}[I] - k_2[I][C]$$

$$= k_1[C][D] - [I](k_{-1} + k_2[C])$$

$$[I] = \frac{k_1[C][D]}{k_{-1} + k_2[C]}$$

$$R = k_2[I][C] = \left[\frac{k_2 k_1[C]^2[D]}{k_{-1} + k_2[C]}\right]$$

(12)  2.  The rate constant for a first order reaction is 0.20 s⁻¹ at 30 °C and 12.40 s⁻¹ at 100 °C.

Calculate the Activation Energy, $E_a$ (in kJ/mol) and the Pre-Exponential Factor, $A$ (in s⁻¹) for this reaction.

$k_1 = 0.20 s^{-1}$

$T_1 = 30°C = 303 K$

$k_2 = 12.45^{-1}$

$T_2 = 100°C = 373 K$

$$\ln(k_2) = \ln A - \frac{E_a}{R}\frac{1}{T_2}$$

$$\ln(k_1) = \ln A - \frac{E_a}{R}\frac{1}{T_1}$$

Subtract equations:

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

$$E_a = \frac{-R \ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-8.31\ J/mol\cdot K\ \ln(12.4/0.20)}{\frac{1}{373K} - \frac{1}{303K}}$$

$$= 55,370\ J/mol \times \frac{1\ kJ}{10^3 J} = \boxed{55.4\ kJ/mol}$$

$$\ln A = \ln k_1 + \frac{E_a}{R}\frac{1}{T_1} = \ln(0.20) + \frac{55,370\ J/mol}{8.31\ J/mol\cdot K}\frac{1}{303K}$$

$$= 20.38$$

$$A = e^{20.38} = \boxed{7.11 \times 10^8\ s^{-1}}$$

(10) 3. An enzyme has the Michaelis-Menten parameters, $K_M = 8.0 \times 10^{-4}$ M and $V_m = 80$ mM/min. The inhibition equilibrium constant for **Competitive** inhibition is $K_I = 2.5 \times 10^{-4}$ M. When [S]= $1.0 \times 10^{-3}$ M, calculate the inhibitor concentration, [I], required to get 80% inhibition (i.e. i%=80) for this **Competitive** inhibitor.

$V_m = 80 \text{ mM/m}$

$K_m = 8 \times 10^{-4} \text{ M}$

$[S] = 1 \times 10^{-3} \text{ M}$

$K_I = 2.5 \times 10^{-4} \text{ M}$

$$i\% = 100\left(1 - \frac{(V_o)_{inh}}{V_o}\right)$$
$$= 80\%$$

$$a\% = 100 - i\% = 20\%$$
$$= 100 \frac{(V_o)_{inh}}{V_o}$$

$$\therefore \frac{(V_o)_{inh}}{V_o} = 0.20$$

$$\frac{V_o}{(V_o)_{inh}} = 5.0 = \frac{\dfrac{V_m [S]}{K_m + [S]}}{\dfrac{V_m [S]}{K_m\left(1 + \frac{[I]}{K_I}\right) + [S]}}$$

$$\frac{V_o}{(V_o)_{inh}} = \frac{1}{0.2} = 5.0$$

$$= \frac{K_m\left(1 + \frac{[I]}{K_I}\right) + [S]}{K_m + [S]} = \frac{K_m + [S]}{K_m + [S]} + \frac{K_m \frac{[I]}{K_I}}{K_m + [S]}$$

$$5.0 = 1.0 + \frac{\frac{K_m}{K_I}[I]}{K_m + [S]} = 1.0 + \frac{\frac{8 \times 10^{-4}}{2.5 \times 10^{-4}}[I]}{8 \times 10^{-4} + 1 \times 10^{-3}}$$

$$5.0 = 1.0 + 1778[I]$$

$$[I] = \frac{5.0 - 1.0}{1778} = 2.25 \times 10^{-3} \text{ M}$$