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# **Constants and Conversion Factors**

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

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)

- A sample of decane, C<sub>10</sub>H<sub>22</sub> (M=142), contains 5.0x10<sup>24</sup> atoms of Hydrogen. What is the mass of the sample?
  - (A) 28.4 g (B) 53.6 g (C) 1180 g (D) 2.6x10<sup>4</sup> g
- 2. The pressure of a sample of O<sub>2</sub>(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<sub>2</sub> (M=44) are contained in a 15 L container at 150 °C and 1.0 bar?
  - (A) 7.2x10<sup>23</sup> (B) 2.6x10<sup>21</sup> (C) 5.8x10<sup>22</sup> (D) 2.6x10<sup>23</sup>
- 4. A sample of C<sub>4</sub>H<sub>10</sub>(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<sub>2</sub>(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<sub>2</sub> 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 , ∆H <0
(C) $w < 0$ , $\Delta H > 0$	(D) w = 0 , ∆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)  $q = -10.3 \text{ kJ}, \Delta H = 0$ (B)  $q = +10.3 \text{ kJ}, \Delta H = 0$ (C)  $q = 0, \Delta H = 0$ (D)  $q = 0, \Delta H = +10.3 \text{ kJ}$
- Zinc reacts with Hydrochloric acid according to the reaction: Zn(s) + HCl(aq) → ZnCl<sub>2</sub>(aq) + H<sub>2</sub>(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<sub>7</sub>H<sub>8</sub>,(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, ∆U, when 230 g of toluene, C<sub>7</sub>H<sub>8</sub>, 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,

	$2 H_2O(g) \rightarrow 2 H_2(g)$	$(g) + O_2(g) \qquad \Delta H =$	⊧ +484 kJ	
	$2 O_3(g) \rightarrow 3 O_2(g)$	) ∆H=	+286 kJ	
$\Delta H$ for the reaction, 3 H <sub>2</sub> O(g) $\rightarrow$ 3 H <sub>2</sub> (g) + O <sub>3</sub> (g), is				
(A) +583 kJ	(B) +341 kJ	(C) -583 kJ	(D) -869 kJ	

- 14. The reaction,  $A \rightarrow B$ , is <u>endergonic</u> at 25 °C and the entropy change is +40 J/K. What can be concluded about the enthalpy change for this reaction?
  - (A)  $\Delta H > +11.9 \text{ kJ}$  (B)  $\Delta H < -11.9 \text{ kJ}$  (C)  $\Delta H > 18.4 \text{ kJ}$

(D) No conclusion can be made about  $\Delta H$ 

15. For the **<u>endergonic</u>** reaction,  $C \rightarrow D$ ,  $\Delta H = -30$  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 <u>system</u> 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 ∆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<sub>3</sub>PO<sub>4</sub> [M=212] is dissolved in 100 grams of water (K<sub>b</sub>=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<sub>4</sub>(I) 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<sub>4</sub>, 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,  $4NO_2(g) + O_2(g) = 2N_2O_5(g)$ . The enthalpy change for this reaction is  $\Delta H^0$  -340 kJ, and the equilibrium constant is K = 8 at 175 °C ( $\Delta G^\circ$  -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) 3.6x10<sup>-2</sup> (D) 4.5x10<sup>-3</sup>

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

27. For the gas phase equilibrium, 2A(g) + B(g) = 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 equilibrium?

**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,  $K_a = 5.0 \times 10^{-10}$ .

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 HCI?

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

OН

ĊH<sub>2</sub>SH

ĊH<sub>2</sub>CO<sub>2</sub>H

The two side groups ionize according to: -CH<sub>2</sub>CO<sub>2</sub>H  $\rightleftharpoons$  H<sup>+</sup> + -CH<sub>2</sub>CO<sub>2</sub> and -CH<sub>2</sub>SH  $\rightleftharpoons$  H<sup>+</sup> + -CH<sub>2</sub>S

The four pKa's are: pKa' ( $\alpha$ -CO<sub>2</sub>H) = 1.9, pKa''( $\beta$ -CO<sub>2</sub>H) = 3.9, pKa'''(CH<sub>2</sub>SH) = 8.5 and pKa''''( $\alpha$ -NH<sub>3</sub><sup>+</sup>) = 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<sup>1+</sup> (B) Pep (C) Pep<sup>1-</sup> (D) Pep<sup>2-</sup>
- 34. The reaction,  $A \rightarrow Products$ , is of order "x"; therefore, the initial rate,  $r_o = k[A]_o^x$ . When  $[A]_o = 0.2 \text{ M}$ ,  $r_o = 0.10 \text{ M/s}$ . When  $[A]_o = 0.8 \text{ M}$ ,  $r_o = 6.40 \text{ M/s}$ . 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,  $k = 0.03 \text{ M}^{-1}\text{s}^{-1}$ . If one starts with an initial concentration,  $[A]_0 = 0.80 \text{ M}$ , 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<sup>-1</sup> (B) 0.07 Ms<sup>-1</sup> (C) 0.29 Ms<sup>-1</sup> (D) 0.035 Ms<sup>-1</sup>
- 37. The reaction, 2NO + O<sub>2</sub> → 2NO<sub>2</sub>, proceeds by a two step mechanism:
  (1) 2NO □ N<sub>2</sub>O<sub>2</sub> (fast pre-equilibrium characterized by the equilibrium constant, K),
  (2) N<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> → 2NO<sub>2</sub> (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)<sup>-1</sup> s.

38 For this reaction, the maximum velocity, V<sub>m</sub>, is

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

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]<sub>0</sub>= 0.05 mM. Therefore, the "turnover number", k<sub>2</sub>, is
  - (A) 1000 s<sup>-1</sup> (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%

### (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:

 $\begin{array}{ccc} k_1 & & k_2 \\ C + D & \square & \mathbf{I} & \text{followed by} & \mathbf{I} + C \longrightarrow P \\ k_{-1} & & \end{array}$ 

"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  $k_2$ .

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

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

(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.