

CHEM 3530 - Final Exam - May 7, 2018

Constants and Conversion Factors

$$R = 8.31 \text{ J/mol-K} = 8.31 \text{ kPa-L/mol-K}$$

$$1 \text{ bar} = 100 \text{ kPa}$$

$$1 \text{ kPa} = 7.50 \text{ torr}$$

$$1 \text{ J} = 1 \text{ kPa-L}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \text{ (Avogadro's Number)}$$

Molar Masses: Given in each question that requires the Molar Mass

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If you wish to have your final exam and course grade posted on the Web site, please provide me with a four (4) digit number which will be the ID number for your grade.

Four (4) digit number for posting.

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

- How many hydrogen atoms are contained in 34 grams of NH_3 ($M=17$)?

(A) 4.0×10^{23} (B) 4.8×10^{34} (C) 1.2×10^{24} (D) 3.6×10^{24}
- The pressure of a sample of $\text{O}_2(\text{g})$ is 150 torr at 200°C in a 10 L container. What is the pressure of this gas at 50°C in a 2 L container?

(A) 1100 torr (B) 510 torr (C) 190 torr (D) 20 torr
- How many grams of $\text{O}_2(\text{g})$ ($M=32$) are contained in a 15.0 L vessel at 0.70 bar and 150°C ?

(A) 9.6 g (B) 0.30 g (C) 26.9 g (D) 0.096 g
- A sample of $\text{CO}_2(\text{g})$ ($M=44$) effuses through a pinhole in 120 s. The same amount of an unknown gas effuses through the pinhole in 160 s. The Molar Mass of the unknown gas is

(A) 78 g/mol (B) 59 g/mol (C) 51 g/mol (D) 25 g/mol
- The constant pressure molar heat capacity of $\text{CO}_2(\text{g})$ is $37.1 \text{ J/mol}\cdot\text{K}$. When 5.0 kJ of heat is added at constant pressure to a 110 g sample of $\text{CO}_2(\text{g})$ ($M=44$) initially at 50°C , the final temperature is

(A) 54°C (B) 68°C (C) 104°C (D) 377°C
- 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) $w = 0$, $\Delta H < 0$
- When a gas is expanded isothermally and reversibly,

(A) $q < 0$ and $\Delta U < 0$ (B) $q < 0$ and $\Delta U = 0$
 (C) $q > 0$ and $\Delta U < 0$ (D) $q > 0$ and $\Delta U = 0$

8. For a process in which the internal energy change of a gas is **positive**, which of the following processes is/are possible?

- (i) the gas is expanded and cooled
 (ii) the gas is compressed and heated
 (iii) the gas is expanded and heated

(A) i only (B) ii only (C) i and iii (D) ii and iii

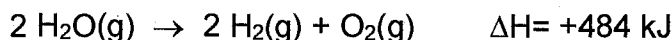
9. What is the work involved when 230 g of liquid toluene, C_7H_8 ($M=92$) is vaporized at 1 bar and $111\text{ }^\circ\text{C}$?

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

10. The enthalpy of vaporization of benzene is 30.8 kJ/mol . What is ΔH when 234 grams of benzene vapor ($M=78$) is condensed to the liquid phase at $80\text{ }^\circ\text{C}$ (its normal boiling point)?

(A) -92.4 kJ (B) -10.3 kJ (C) +92.4 kJ (D) -8.8 kJ

11. From the following thermochemical equations,



ΔH for the reaction, $3\text{ H}_2(\text{g}) + \text{O}_3(\text{g}) \rightarrow 3\text{ H}_2\text{O}(\text{g})$ is

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

12. The constant pressure molar heat capacity of $\text{N}_2(\text{g})$ is $29.1\text{ J/mol}\cdot\text{K}$. What is the entropy change when 4 moles of N_2 are heated from $50\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$ at 1 bar?

(A) +161 J/K (B) +23.2 J/K (C) +44.4 J/K (D) +11.1 J/K

13. A sample of 0.5 moles of $\text{O}_2(\text{g})$ originally at 500 kPa and 5 L is expanded reversibly and isothermally to a final volume of 25 L. What is ΔS for this process?

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

14. The normal melting point of toluene is $-95\text{ }^\circ\text{C}$. The enthalpy of fusion of toluene is 6.6 kJ/mol . What is the entropy change of the **system** when one mole of solid toluene melts to liquid toluene at $-95\text{ }^\circ\text{C}$?

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

15. The enthalpy of fusion of ~~chloroform~~ mercury is 2.3 kJ/mol . What is the entropy change of the **surroundings** when 4 moles of mercury liquid are frozen (i.e. crystallized) to the solid at $-39\text{ }^\circ\text{C}$?

(A) +9.8 J/K (B) +39.3 J/K (C) -9.8 J/K (D) -39.3 J/K

16. The entropy change for the **endergonic** reaction, $A \rightarrow B$, is $+120 \text{ J/K}$. What can you say about the enthalpy change for this reaction at $27 \text{ }^\circ\text{C}$?

- (A) $\Delta H > +36 \text{ kJ}$ (B) $\Delta H > -36 \text{ kJ}$ (C) $\Delta H < +36 \text{ kJ}$
(D) Insufficient information is available

17. For the **exergonic** reaction, $C \rightarrow D$, $\Delta H = +25 \text{ kJ}$. For this reaction,

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

18. When 60 grams of glucose ($M=180$) is added to 150 grams of water ($M=18$), the density of the solution is 1.15 g/mL . What is the Molarity of the above solution?

- (A) 2.6 Molar (B) 2.4 Molar (C) 2.2 Molar (D) 1.8 Molar

19. When 37 grams of the strong electrolyte, $\text{Mg}(\text{NO}_3)_2$ [$M=148$], is dissolved in 125 grams of H_2O ($K_f 1.9 \text{ }^\circ\text{C/m}$), the freezing point of the solution is:

- (A) $-11.4 \text{ }^\circ\text{C}$ (B) $+3.8 \text{ }^\circ\text{C}$ (C) $-7.6 \text{ }^\circ\text{C}$ (D) $-3.8 \text{ }^\circ\text{C}$

20. When 25 grams of an unknown compound is dissolved in 500 g of water ($K_f=1.9 \text{ }^\circ\text{C/m}$), the freezing point of the solution is $-1.10 \text{ }^\circ\text{C}$. The Molar Mass of the compound is approximately

- (A) 58 g/mol (B) 29 g/mol (C) 105 g/mol (D) 86 g/mol

21. When 2.0 grams of sucrose ($M = 342$) is dissolved in 500 mL of aqueous solution, what is the osmotic pressure of the solution at $60 \text{ }^\circ\text{C}$, in bar?

- (A) 0.06 bar (B) 0.32 bar (C) 5.8 bar (D) 32.4 bar

For #22 - #26: Consider the gas phase equilibrium, $2 \text{ POCl}_3(\text{g}) = 2 \text{ PCl}_3(\text{g}) + \text{O}_2(\text{g})$. The enthalpy change for this reaction is $+510 \text{ kJ}$, and the equilibrium constant at $27 \text{ }^\circ\text{C}$ is $K = 25$.

22. For the above reaction, if the temperature is **decreased**,

- (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 volume 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 ΔG for this reaction at 27 °C when $P_{\text{POCl}_3} = 0.1$ bar and $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 3.0$ bar?

- (A) -8.0 kJ (B) -19.7 kJ (C) +11.7 kJ (D) +19.7 kJ

25. For the reaction, $\text{PCl}_3(\text{g}) + (1/2) \text{Cl}_2(\text{g}) = \text{POCl}_3(\text{g})$, the equilibrium constant at 27 °C is

- (A) 0.20 (B) 0.04 (C) 5.0 (D) 1.6×10^{-3}

26. What is the value of the equilibrium constant for the original reaction, $\text{POCl}_3(\text{g}) = 2 \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, at 47 °C?

- (A) 7.0×10^{-5} (B) 2.6×10^4 (C) 100 (D) 8.9×10^6

27. The gas phase molecule, A, dissociates according to the equilibrium,

$\text{A}(\text{g}) = \text{B}(\text{g}) + 3 \text{C}(\text{g})$. The equilibrium constant is 1×10^{-3} . If one puts an initial pressure of 5 bar of A into a flask, what is the pressure of B at equilibrium?

[NOTE: You may assume that very little A dissociates]

- (A) 0.27 bar (B) 0.12 bar (C) 0.08 bar (D) 0.36 bar

For #28 - #30: Pyridine (Pyr) is a weak base with a base equilibrium constant, $K_b = 1.7 \times 10^{-9}$.

28. What is the approximate pH of a 0.20 M solution of pyridine (Pyr)?

- (A) 9.3 (B) 4.7 (C) 4.4 (D) 9.6

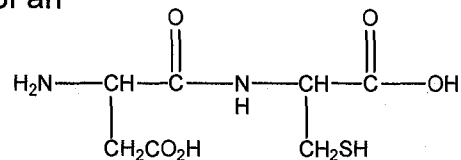
29. What is the approximate pH of a 0.04 M solution of pyridinium chloride (PyrHCl)?

- (A) 3.3 (B) 5.1 (C) 8.9 (D) 10.7

30. What is the approximate pH after 120 mL of 1.00 M of NaOH is added to 500 mL of a 0.40 M solution of aqueous pyridinium chloride?

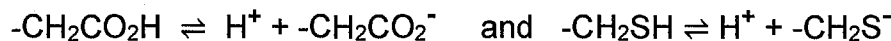
- (A) 9.0 (B) 5.1 (C) 8.6 (D) 5.4

For #31 - #33: Consider the dipeptide (Pep) consisting of an Aspartic Acid residue and a Cysteine residue (pictured on right)



Note: The most positive form of the peptide has a charge of +1

The two side groups ionize according to:



The four pK_a 's are: pK_a' (α -CO₂H) = 1.9, pK_a'' (β -CO₂H) = 3.9, pK_a''' (CH₂SH) = 8.5 and pK_a'''' (α -NH₃⁺) = 9.9

31. 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
32. What pH corresponds to the isoelectric point, pI , of Pep?
- (A) 2.9 (B) 3.9 (C) 6.2 (D) 9.2
33. What is the average charge of Pep at pH = 8.5?
- (A) -2.5 (B) -0.5 (C) -2.0 (D) -1.5
34. Consider a 5/2 order reaction; i.e. $R = k[A]^{5/2}$. When the initial concentration is $[A_0] = 0.05 \text{ M}$, the initial rate is $12. \text{ Ms}^{-1}$. What is the approximate value of the rate constant (in units of $\text{M}^{-3/2}\text{s}^{-1}$) ?
- (A) 4.7×10^{-5} (B) 6.7×10^{-3} (C) $1.1 \times 10^{+5}$ (D) $2.1 \times 10^{+4}$
35. The reaction, $A \rightarrow \text{Products}$, is of order "x"; i.e. $\text{rate} = k[A]^x$. When $[A_0] = 0.25 \text{ M}$, the half-life of the reaction is 400 s. When $[A_0] = 0.50 \text{ M}$, the half life of the reaction is 100 s. The order of the reaction, x, is
- (A) 4 (B) 3 (C) 2 (D) -2
36. Consider the second order reaction, $A \rightarrow \text{Products}$. The rate constant is $k = 0.10 \text{ M}^{-1}\text{s}^{-1}$, and the initial concentration is $[A]_0 = 0.50 \text{ M}$. What is the concentration of A 30 seconds after the start of the reaction?
- (A) 0.20 M (B) 0.125 M (C) 0.24 M (D) 0.36 M
37. A reaction proceeds by the two step mechanism: (1) $A_2 \rightleftharpoons 2 A$ (fast pre-equilibrium, characterized by the equilibrium constant, K) and (2) $A + B \rightarrow \text{Product}$ (Slow Rate-Determining Step, characterized by rate constant, k). The rate law for the formation of product is of the form:
- (A) $k_{\text{eff}}[A_2]^2[B]$ (B) $k_{\text{eff}}[A_2][B]$ (C) $k_{\text{eff}}[A_2]^{1/2}[B]$ (D) $k_{\text{eff}}[A_2][B]^{1/2}$

38. For an enzyme catalyzed reaction, when the substrate concentration, $[S] = 3K_M$, then the initial velocity, v_0 is

- (A) $0.25V_m$ (B) $0.67 V_m$ (C) $0.75V_m$ (D) $1.33V_m$

For #39 - #40: Consider an enzyme catalyzed reaction with $[E]_0 = 2 \text{ mM}$, $K_M = 20 \text{ mM}$, and $V_M = 80 \text{ mM/s}$

39. The slope of the Lineweaver-Burk plot is

- (A) 0.013 s/mM (B) 4 s^{-1} (C) $6.3 \times 10^{-4} \text{ mM/s}$ (D) 0.25 s

40. The intercept of the Lineweaver-Burk plot is

- (A) 0.013 s/mM (B) 4 s^{-1} (C) $6.3 \times 10^{-4} \text{ mM/s}$ (D) 0.25 s

41. When an inhibitor is added to an enzyme catalyzed reaction, it is found that the slope of the Lineweaver-Burk plot is increased, but the intercept remains unchanged. Therefore, the type of inhibition is

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

For #42 - #43: Consider an enzyme catalyzed reaction with $K_M = 25 \text{ mM}$, $V_m = 100 \text{ } \mu\text{M/s}$, and $[S] = 40 \text{ mM}$. A **Competitive** inhibitor to this reaction has an inhibitor constant, $K_I = 10 \text{ mM}$.

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

- (A) 62 mM/s (B) 54 mM/s (C) 38 mM/s (D) 83 mM/s

43. What is the percent inhibition ($i\%$) when the inhibitor concentration is $[I] = 30 \text{ mM}$?

- (A) 36% (B) 46% (C) 54% (D) 64%

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

(08) 1. The reaction, $2B + C \rightarrow P$ (P is the product) proceeds by the following mechanism.



"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 [B], [C], k_1 , k_{-1} and k_2 .

Steady-state on [I]

$$\frac{d[I]}{dt} = 0 = +k_1 [B]^2 - k_{-1} [I] - k_2 [I][C]$$

$$0 = k_1 [B]^2 - [I](k_{-1} + k_2 [C])$$

$$\therefore [I] = \frac{k_1 [B]^2}{k_{-1} + k_2 [C]}$$

$$R_p = \frac{d[P]}{dt} = k_2 [I][C]$$

$$= \frac{k_2 k_1 [B]^2 [C]}{k_{-1} + k_2 [C]}$$

- (10) 2. The rate constant for a first order reaction is 2.5 s^{-1} at 30°C and the Activation Energy is 75 kJ/mol . Calculate the temperature, in $^\circ\text{C}$, at which the rate constant will be $100. \text{ s}^{-1}$.

$$E_a = 75 \text{ kJ/mol} = 7.5 \times 10^4 \text{ J/mol}$$

$$k_1 = 2.5 \text{ s}^{-1}$$

$$T_1 = 30^\circ\text{C} = 303 \text{ K}$$

$$k_2 = 100 \text{ s}^{-1}$$

$$T_2 = ?$$

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

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

$$\begin{aligned} \therefore \frac{1}{T_2} &= \frac{1}{T_1} - \frac{R}{E_a} \ln\left(\frac{k_2}{k_1}\right) \\ &= \frac{1}{303 \text{ K}} - \frac{8.314 \text{ J/mol}\cdot\text{K}}{7.5 \times 10^4 \text{ J/mol}} \ln \frac{100}{2.5} \\ &= 2.892 \times 10^{-3} \text{ K}^{-1} \end{aligned}$$

$$T_2 = \frac{1}{2.892 \times 10^{-3} \text{ K}^{-1}} = 345.8 \text{ K} = 346 \text{ K}$$

$$= 73^\circ\text{C}$$

- (12) 3. An enzyme has the Michaelis-Menten parameters, $K_M = 60 \text{ mM}$ and $V_m = 100 \text{ } \mu\text{M}/\text{min}$. The inhibition equilibrium constant for **Uncompetitive** inhibition is $K_I = 10 \text{ mM}$. When $[S] = 30 \text{ mM}$, calculate the inhibitor concentration, $[I]$, in **mM**, required to get 75% inhibition (i.e. $i\% = 75$) for this **Uncompetitive** inhibitor.

$$\text{also } 100 - i\% = 25\% = \frac{(V_0)_i}{V_0} \times 100$$

$$\frac{(V_0)_i}{V_0} = 0.25 \rightarrow \frac{V_0}{(V_0)_i} = \frac{1}{0.25} = 4.0$$

$$\frac{V_0}{(V_0)_i} = 4 = \frac{\frac{V_m [S]}{K_M + [S]}}{\frac{V_m [S]}{K_M + [S] + \frac{[S][I]}{K_I}}} = \frac{K_M + [S] + \frac{[S][I]}{K_I}}{K_M + [S]}$$

$$4 = \frac{K_M + [S] + \frac{[S][I]}{K_I}}{K_M + [S]} = 1 + \frac{\frac{[S][I]}{K_I}}{K_M + [S]}$$

$$4 = 1 + \frac{30 [I]}{\frac{10}{60 + 30}} = 1 + 0.0333 [I]$$

$$[I] = \frac{4 - 1}{0.0333} = \boxed{90 \text{ mM}}$$