

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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Name _____

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,
- $$2\text{ H}_2\text{O}(\text{g}) \rightarrow 2\text{ H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = +484\text{ kJ}$$
- $$2\text{ O}_3(\text{g}) \rightarrow 3\text{ O}_2(\text{g}) \quad \Delta H = +286\text{ kJ}$$
- 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

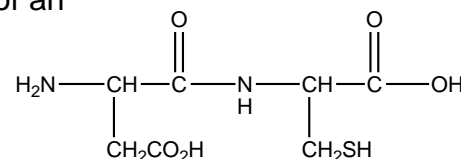
16. The entropy change for the **endergonic** reaction, $A \rightarrow B$, is $+120 \text{ J/K}$. What can you say about the enthalpy change for this reaction at $27 \text{ }^\circ\text{C}$?
- (A) $\Delta H > +36 \text{ kJ}$ (B) $\Delta H > -36 \text{ kJ}$ (C) $\Delta H < +36 \text{ kJ}$
 (D) Insufficient 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

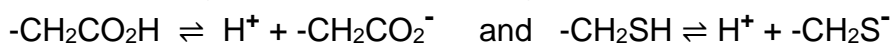
24. What is ΔG for this reaction at 27 °C when $P_{\text{POCl}_3} = 0.1$ bar and $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 3.0$ bar?
(A) -8.0 kJ (B) -19.7 kJ (C) +11.7 kJ (D) +19.7 kJ
25. For the reaction, $\text{PCl}_3(\text{g}) + (1/2) \text{Cl}_2(\text{g}) = \text{POCl}_3(\text{g})$, the equilibrium constant 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? 2
(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 - CO_2H) = 1.9, pK_a'' (β - CO_2H) = 3.9, pK_a''' (CH_2SH) = 8.5 and pK_a'''' (α - NH_3^+) = 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 $\text{pH} = 8.5$?
- (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 .

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

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