

Name: _____

CHEM3142 PHYSICAL CHEMISTRY: EXAM II

Monday March 20th 2006 Time: 110 Minutes

89 points total

Answer all questions in detail and SHOW ALL WORK! Please write answers on your paper.

Planck's constant $h = 6.626 \times 10^{-34}$ Js speed of light $c = 2.998 \times 10^8$ ms⁻¹
 Avogadro's number = 6.022×10^{23} mol⁻¹

KEY

1 Pa = 1 N m⁻² = 1 J m⁻³ = 1 Kg m⁻¹ s⁻² 1 J = 1 kg m² s⁻²
 760 Torr = 101325 Pa = 1 atm (exactly) = 1.01325 bar
 1 L = 1 dm³ = 1000 cm³ = 10⁻³ m³
 R = 8.31451 J K⁻¹ mol⁻¹ = 0.0831451 dm³ bar K⁻¹ mol⁻¹ = 0.0820578 dm³ atm K⁻¹ mol⁻¹
 Planck's constant $h = 6.626 \times 10^{-34}$ Js speed of light $c = 2.998 \times 10^8$ ms⁻¹
 $k_B = 1.380658 \times 10^{-23}$ J K⁻¹ $\tilde{k}_B = 0.695038$ cm⁻¹ K⁻¹ electron's mass $m_e = 9.109 \times 10^{-31}$ Kg
 1 cm⁻¹ = 1.986×10^{-23} J 1 eV = 1.602×10^{-19} J 350 cm⁻¹ = 1 Kcal mol⁻¹

Equations & Formulae

1. First Law + Total differential of U(V,T):

$$dU = dq + dw = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

2. Enthalpy physical changes.

Definition of Enthalpy + Total differential of H(P,T)

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = dU + PdV + VdP = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

3. Entropy physical changes

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

4. Fundamental Equations

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

5. ΔG and K_p for $aA + bB \rightarrow eE + fF$ gas phase rxn of ideal gases

$$\Delta G = \Delta G^0 + RT \ln \frac{P_E^e P_F^f}{P_A^a P_B^b} = \Delta G^0 + RT \ln Q_p$$

but $Q_p = \text{proper quotient of pressures}$

AT Equilibrium $Q_p = K_p$

note: $P_i = \text{short for } \frac{P_i}{P^0} \text{ in bar units}$

$$P^0 = 1 \text{ bar}$$

1. (4 pts) The fugacity coefficient γ , is given by $\gamma = \frac{f}{P}$ where f = fugacity and P is pressure. Which of the following statements is true.

- As the pressure approaches zero γ approaches 1.
- As the pressure approaches zero γ approaches ∞ .
- $f \sim P$ at high pressures
- As the fugacity approaches zero γ approaches 0.

2. (4 pts) In the Gibbs Phase Rule the degrees of freedom (f) is specified as a function of the number of phases (p) and number of components (c): $f = c - p + 2$ For a single component phase diagram, what is the value of f along the liquid-solid coexistence curve.

- 1
- 0
- 1
- 2

3. (4 pts) A solid-liquid coexistence curve which falls from left-to-right in the P vs T phase diagram

consistent with $\frac{dP}{dT} = \frac{D_{fus} \bar{H}}{T D_{fus} \bar{V}}$ indicates:

- $\bar{V}^l - \bar{V}^s > 0$
- $\frac{dP}{dT} < 0$
- $T < 0$.
- $D_{fus} \bar{H} > 0$

For problems 4 – 7 explicitly show ALL WORK!

4. (10 Pts) Use the Maxwell relation $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ and the total differential

$dH = TdS + VdP$ to show that $\left(\frac{\partial H}{\partial P}\right)_T = 0$ for an ideal gas.

5. (52 Pts) Answer the following questions by making use of the table below (entries given at 298.15 K, 1 bar). Assume ideal gas behavior, assume that no phase changes are involved.

Substance	$D_f \bar{H}^0 / \text{kJ mol}^{-1}$	$\bar{S}^0 / \text{J K}^{-1} \text{mol}^{-1}$	$\bar{C}_p^0 / \text{J K}^{-1} \text{mol}^{-1}$
NO ₂ (g)	33.2	239.9	37.18
N ₂ O ₄ (g)	9.16	304.3	79.20

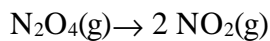
(a) (7 pts) Compute $\bar{S}^0(\text{NO}_2(\text{g}), 398.15 \text{ K})$ 1 bar utilizing:

$$\bar{S}^0(\text{NO}_2(\text{g}), 398.15 \text{ K}) = \bar{S}^0(\text{NO}_2(\text{g}), 298.15 \text{ K}) + D\bar{S}^0 \quad (\text{assume } C_p^0 \text{ is constant}).$$

(b) (7 pts) Compute $\bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 2.50 \text{ bar})$ at 298.15 K utilizing:

$$\bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 2.50 \text{ bar}) = \bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 1.00 \text{ bar}) + D\bar{S}^0 \quad (\text{assume ideal gas}).$$

(c) (10 pts) Calculate $D_{rxn} \bar{S}^0$ and $D_{rxn} \bar{H}^0$ at 298.15 K and 1 bar for the reaction:



(d) (5 pts) Use the values of $D_{rxn} \bar{S}^0$ and $D_{rxn} \bar{H}^0$ in part c to confirm that $\Delta_{rxn} \bar{G}^0 = 4.92 \text{ kJ mol}^{-1}$

(e) (5 pts) Determine K_p from the value of $\Delta_{rxn} \bar{G}^0 = 4.92 \text{ kJ mol}^{-1}$.

(f) (5 pts) If the equilibrium partial pressure of NO₂ is 0.3 bar, what is the equilibrium partial pressure of N₂O₄.

(g) (5 Pts) If initially $P(\text{N}_2\text{O}_4(\text{g})) = 0.5000 \text{ bar}$, and $P(\text{NO}_2(\text{g})) = 0.250 \text{ bar}$ will the reaction proceed spontaneously from left-to-right. Justify your answer.

(h) (8 pts) Complete the following table utilizing symbols: 0.250, ξ , and P (equilibrium total pressure)

	N ₂ O ₄ (g)	NO ₂ (g)
Initial moles	0.250	0
Change moles in units of ξ (extent of reaction)		
Final moles at equilibrium		
Mole fraction		
Partial Pressure		

6. (5 Pts) Starting with **one** of the fundamental equations (see #4 under "Equations & Formulae" on

1st page) Prove the following Maxwell relation:
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

7. (8 Pts) The normal boiling point (boiling point at barometric pressure of 1 atm) of diethyl ether is 34.5°C, and its $D_{vap}\bar{H}$ is 26.69 kJ mol⁻¹. Determine the vapor pressure of diethyl ether at 25°C via the Clausius-Clapeyron equation:

$$\ln \frac{P_2}{P_1} = -\frac{D_{vap}\bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

ANSWER KEY

1. (4 pts) The fugacity coefficient γ , is given by $\gamma = \frac{f}{P}$ where f = fugacity and P is pressure. Which of the following statements is true.

- a.** As the pressure approaches zero γ approaches 1. **(THIS WAS A QUIZ QUESTION!)**
- b. As the pressure approaches zero γ approaches ∞ .
- c. $f \sim P$ at high pressures
- d. As the fugacity approaches zero γ approaches 0.

2. (4 pts) In the Gibbs Phase Rule the degrees of freedom (f) is specified as a function of the number of phases (p) and number of components (c): $f = c - p + 2$ For a single component phase diagram, what is the value of f along the liquid-solid coexistence curve.

- a. -1
- b. 0
- c. 1**
- d. 2

3. (4 pts) A solid-liquid coexistence curve which falls from left-to-right in the P vs T phase diagram

consistent with $\frac{dP}{dT} = \frac{D_{fus} \bar{H}}{TD_{fus} \bar{V}}$ indicates:

- a. $\bar{V}^l - \bar{V}^s > 0$
- b.** $\frac{dP}{dT} < 0$
- c. $T < 0$.
- d. $D_{fus} \bar{H} > 0$

4. (10 Pts) Use the Maxwell relation $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ and the total differential

$dH = TdS + VdP$ to show that $\left(\frac{\partial H}{\partial P}\right)_T = 0$ for an ideal gas.

ANSWER: Divide both sides by dP at constant T: $\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V$

Applying the Maxwell Relation:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V \quad \text{Ideal gas } V = \frac{nRT}{P}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V = -T \left(\frac{\partial}{\partial T} \left(\frac{nRT}{P}\right)\right)_P + V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{nR}{P}\right) + V = -V + V = 0$$

I worked this problem during the problem session for Lecture #19!

5. (52 Pts) Answer the following questions by making use of the table below (entries given at 298.15 K, 1 bar). Assume ideal gas behavior, assume that no phase changes are involved.

Substance	$D_f \bar{H}^0 / \text{kJ mol}^{-1}$	$\bar{S}^0 / \text{J K}^{-1} \text{mol}^{-1}$	$\bar{C}_p^0 / \text{J K}^{-1} \text{mol}^{-1}$
NO ₂ (g)	33.2	239.9	37.18
N ₂ O ₄ (g)	9.16	304.3	79.20

(a) (7 pts) Compute $\bar{S}^0(\text{NO}_2(\text{g}), 398.15 \text{ K})$ 1 bar utilizing:

$$\bar{S}^0(\text{NO}_2(\text{g}), 398.15 \text{ K}) = \bar{S}^0(\text{NO}_2(\text{g}), 298.15 \text{ K}) + D\bar{S}^0 \quad (\text{assume } C_p^0 \text{ is constant}).$$

$$dS = \frac{C_p}{T} dT - \frac{\alpha \int V \ddot{\alpha}}{\xi \int T \theta_p} dP \quad \text{constant } P \quad \Rightarrow \quad d\bar{S} = \frac{\bar{C}_p}{T} dT \quad \Rightarrow \quad D\bar{S} = \bar{C}_p \int_{T_1}^{T_2} \frac{dT}{T} = \bar{C}_p \ln \frac{T_2}{T_1}$$

$$D\bar{S} = 37.18 \text{ JK}^{-1} \text{mol}^{-1} \ln \frac{398.15 \text{ K}}{298.15 \text{ K}} = 10.75 \text{ JK}^{-1} \text{mol}^{-1}$$

$$\bar{S}^0(\text{NO}_2(\text{g}), 398.15 \text{ K}) = 239.9 \text{ JK}^{-1} \text{mol}^{-1} + 10.75 \text{ JK}^{-1} \text{mol}^{-1} = 250.65 \text{ JK}^{-1} \text{mol}^{-1}$$

(b) (7 pts) Compute $\bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 2.50 \text{ bar})$ at 298.15 K utilizing:

$$\bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 2.50 \text{ bar}) = \bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 1.00 \text{ bar}) + D\bar{S}^0 \quad (\text{assume ideal gas}).$$

$$dS = \frac{C_p}{T} dT - \frac{\alpha \int V \ddot{\alpha}}{\xi \int T \theta_p} dP \quad \text{constant } T \quad \Rightarrow \quad dS = - \frac{\alpha \int V \ddot{\alpha}}{\xi \int T \theta_p} dP \quad \Rightarrow \quad V = \frac{nRT}{P}$$

$$\frac{\alpha \int V \ddot{\alpha}}{\xi \int T \theta_p} = \frac{nR}{P} \quad \Rightarrow \quad dS = - \frac{nR}{P} dP \quad \Rightarrow \quad D\bar{S} = - nR \ln \frac{P_2}{P_1} \quad \Rightarrow \quad D\bar{S} = R \ln \frac{P_1}{P_2}$$

$$D\bar{S} = 8.3145 \text{ JK}^{-1} \text{mol}^{-1} \ln \frac{1 \text{ bar}}{2.5 \text{ bar}} = -7.618 \text{ JK}^{-1} \text{mol}^{-1}$$

$$\bar{S}^0(\text{N}_2\text{O}_4(\text{g}), 2.50 \text{ bar}) = 304.3 \text{ JK}^{-1} \text{mol}^{-1} + -7.618 \text{ JK}^{-1} \text{mol}^{-1} = 296.68 \text{ JK}^{-1} \text{mol}^{-1}$$

(c) (10 pts) Calculate $D_{rxn} \bar{S}^0$ and $D_{rxn} \bar{H}^0$ at 298.15 K and 1 bar for the reaction:

$$\text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$$

$$D_{rxn} \bar{S}^0 = 2 \times \bar{S}^0(\text{NO}_2) - \bar{S}^0(\text{N}_2\text{O}_4(\text{g})) = 2 \times 250.65 \text{ JK}^{-1} \text{mol}^{-1} - 304.3 \text{ JK}^{-1} \text{mol}^{-1} = 175.5 \text{ JK}^{-1} \text{mol}^{-1}$$

$$D_{rxn} \bar{H}^0 = 2 \times D_f \bar{H}^0(\text{NO}_2) - D_f \bar{H}^0(\text{N}_2\text{O}_4(\text{g})) = 2 \times 33.2 \text{ kJ mol}^{-1} - 9.16 \text{ kJ mol}^{-1} = 57.24 \text{ kJ mol}^{-1}$$

(d) (5 pts) Use the values of $D_{rxn} \bar{S}^0$ and $D_{rxn} \bar{H}^0$ in part c to confirm that $\Delta_{rxn} \bar{G}^0 = 4.92 \text{ kJ mol}^{-1}$

$$D_{rxn} \bar{G}^0 = D_{rxn} \bar{H}^0 - T D_{rxn} \bar{S}^0 = 57.24 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times 175.5 \text{ JK}^{-1} \text{mol}^{-1} = 4.92 \text{ kJ mol}^{-1}$$

(e) (5 pts) Determine K_p from the value of $\Delta_{rxn} \bar{G}^0 = 4.92 \text{ kJ mol}^{-1}$.

$$DG = DG^0 + RT \ln Q_p \quad \rightarrow \text{at equilibrium} \quad \rightarrow \quad 0 = DG^0 + RT \ln K_p \quad \Rightarrow \quad K_p = \exp \left\{ - \frac{DG^0}{RT} \right\}$$

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{4920 \text{ J mol}^{-1}}{8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 298.15 \text{ K}}\right) = 0.137$$

(f) (5 pts) If the equilibrium partial pressure of NO₂ is 0.3 bar, what is the equilibrium partial pressure of N₂O₄.

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \quad \text{or} \quad P_{\text{N}_2\text{O}_4} = \frac{P_{\text{NO}_2}^2}{K_p} = \frac{(0.3 \text{ bar})^2}{0.137(\text{bar})} = 0.675 \text{ bar}$$

(g) (5 Pts) If initially P(N₂O₄(g)) = 0.5000 bar, and P(NO₂(g)) = 0.250 bar will the reaction proceed spontaneously from left-to-right. Justify your answer.

$$\Delta G = \Delta G^\circ + RT \ln Q_p = -RT \ln K_p + RT \ln Q_p = RT \ln \frac{Q_p}{K_p} = RT \ln \frac{0.25^2}{0.5 \cdot 0.137}$$

$$\Delta G = RT \ln \frac{0.125}{0.137} < 0 \quad \text{or} \quad \text{yes spontaneous since } \Delta G < 0$$

(h) (8 pts) Complete the following table utilizing symbols: 0.250, ξ, and P (equilibrium total pressure)

	N ₂ O ₄ (g)	NO ₂ (g)
Initial moles	0.250	0
Change moles in units of ξ (extent of reaction)	-ξ	+2ξ
Final moles at equilibrium	0.250 - ξ	2ξ
Mole fraction	(0.250 - ξ) / (0.250 + ξ)	(2ξ) / (0.250 + ξ)
Partial Pressure	(0.250 - ξ)P / (0.250 + ξ)	(2ξ)P / (0.250 + ξ)

6. (5 Pts) Starting with the fundamental equations (see #4 under "Equations & Formulae" on 1st

page) Prove the following Maxwell relation: $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

Since dG is an exact differential the mixed derivative are equal:

$$\left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial P}\right)_T \rightarrow \left(\frac{\partial}{\partial P}\right)_T (-S) = \left(\frac{\partial}{\partial T}\right)_P (V) \rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

7. (8 Pts) The normal boiling point (boiling point at barometric pressure of 1 atm) of diethyl ether is 34.5°C, and its $D_{\text{vap}} \bar{H}$ is 26.69 kJ mol⁻¹. Determine the vapor pressure of diethyl ether at 25°C via the

Clausius-Clapeyron equation:

$$\ln \frac{P_2}{P_1} = - \frac{D_{vap} \bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \Rightarrow \frac{P_2}{P_1} = \exp \left(- \frac{D_{vap} \bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$

$$P_2 = P_1 \exp \left(- \frac{D_{vap} \bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right) = 1 \text{ atm} \exp \left(- \frac{26690 \text{ J mol}^{-1}}{8.3145 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{1}{298.15} - \frac{1}{307.65} \right) \right)$$

$$P_2 = 1 \text{ atm} \cdot \exp \left(- \frac{26690 \text{ J mol}^{-1}}{8.3145 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{1}{298.15} - \frac{1}{307.65} \right) \right) = 0.721 \text{ atm}$$