

CHEM 5200 - Exam 1 - September 26, 2017

INFORMATION PAGE (Use for reference and for scratch paper)

Constants and Conversion Factors:

$$R = 0.082 \text{ L-atm/mol-K} = 8.31 \text{ J/mol-K} = 8.31 \text{ kPa-L/mol-K}$$

$$1 \text{ L-atm} = 101 \text{ J}$$

$$1 \text{ L-bar} = 100 \text{ J}$$

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

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

$$1 \text{ atm} = 760 \text{ torr}$$

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ Pa}$$

Relations for Adiabatic Expansions and Compressions of a Perfect Gas

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{R/C_{v,m}} \quad \text{or} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{C_{p,m}/C_{v,m}} = \left(\frac{V_1}{V_2} \right)^\gamma \quad \gamma = \frac{C_{p,m}}{C_{v,m}}$$

CHEM 5200 - Exam 1 - September 26, 2017

Name Soh Young

(27) MULTIPLE CHOICE [3 points per question] (Circle the ONE correct answer)

- What are w and ΔU when 3. moles of a gas is compressed isothermally and reversibly from 30 L to 2 L at 50 °C?

(A) $w=0$ and $\Delta U=+21.8$ kJ (B) $w=-21.8$ kJ and $\Delta U=0$
 (C) $w=+21.8$ kJ and $\Delta U=-21.8$ kJ (D) $w=+21.8$ kJ and $\Delta U=0$
- When a gas is cooled at constant volume,

(A) $\Delta U < 0$ & $w < 0$ (B) $\Delta U < 0$ & $w > 0$ (C) $\Delta U > 0$ & $w = 0$ (D) $\Delta U < 0$ & $w = 0$
- Solid Nickel reacts with gaseous carbon monoxide to form solid nickel tetracarbonyl according to the equation. $\text{Ni}(\text{sol}) + 4 \text{CO}(\text{gas}) \rightarrow \text{Ni}(\text{CO})_4(\text{liq})$. What is the work involved when 3. moles of Ni(sol) react with CO(gas) to form Ni(CO)₄(liq) at 100 °C and 1 bar pressure?

(A) +12.4 kJ (B) +37.2 kJ (C) -12.4 kJ (D) -37.2 kJ
- The molar constant volume heat capacity of CO₂(g) is constant at $C_{v,m} = 28.2$ J/mol-K. You can assume that CO₂(g) is a Perfect Gas. When 4. moles of CO₂(g) is heated from 100 °C to 250 °C,

(A) $\Delta H = +11.9$ kJ & $\Delta U = +16.9$ kJ (B) $\Delta H = +16.9$ kJ & $\Delta U = +21.9$ kJ
 (C) $\Delta H = +5.5$ kJ & $\Delta U = +4.2$ kJ (D) $\Delta H = +21.9$ kJ & $\Delta U = +16.9$ kJ
- The **constant pressure** molar heat capacity of a Perfect Gas is: $C_{p,m} = 21.0$ J/mol-K. When a sample of this gas originally at a pressure of 2. bar and volume of 50. L is **compressed adiabatically and reversibly** to a final volume of 20. L. What is the approximate final pressure of the gas?

(A) 4.6 bar (B) 5.0 bar (C) 7.2 bar (D) 9.1 bar
- For the reaction, $2 \text{SO}_3(\text{g}) \rightarrow 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$, $\Delta H^\circ = +200$ kJ. The Enthalpy of Formation of SO₃(g) is -397 kJ/mol. What is the Enthalpy of Formation of SO₂(g)?

(A) -297 kJ (B) +497 kJ (C) -497 kJ (D) +297 kJ
- What is the work involved when five(5) moles of liquid chlorobenzene vaporizes to the gas at its boiling point, 131 °C ?

(A) -16.8 kJ (B) +3.4 kJ (C) -3.4 kJ (D) +16.8 kJ

8. The thermal expansion coefficient of a substance is defined by:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

Consider a hypothetical gas which follows the Equation of State:

$$pV = nRT^2$$

The thermal expansion coefficient of this hypothetical gas is given by:

- (A) $\frac{2nRT}{p}$ (B) $\frac{2}{T}$ (C) $\frac{2}{p}$ (D) $\frac{3}{T}$

9. The internal pressure is defined by, $\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$, and is a measure of attractive or repulsive forces between molecules in real gases. Consider a gas in which **attractive** interactions between molecules predominate. When one mole of this gas is compressed isothermally from 1 bar pressure to 10 bar pressure:

(A) $\pi_T > 0, \Delta U > 0$

(B) $\pi_T < 0, \Delta U > 0$

(C) $\pi_T > 0, \Delta U < 0$

(D) $\pi_T < 0, \Delta U < 0$

FIVE(5) PROBLEMS on following pages:

NOTE: You Must show your work to receive credit.

(11) 1. Starting with the total differential for $V(p,T)$, prove that: $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$,

where $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ and $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$

You MUST show all steps to receive credit on this derivation.

$V(p,T): dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$

Divide by dT . $\frac{dV}{dT} = \left(\frac{\partial V}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial V}{\partial T}\right)_p$

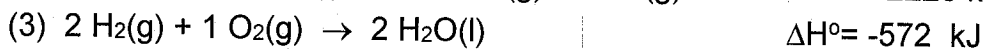
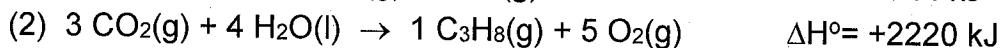
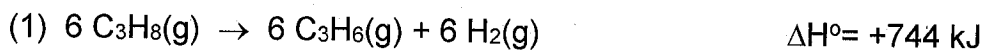
Hold V const $0 = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p$

Solve for $\left(\frac{\partial p}{\partial T}\right)_V = \frac{-\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$

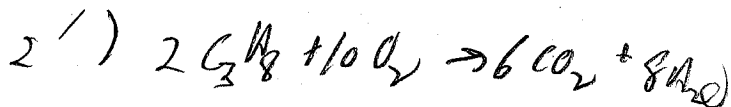
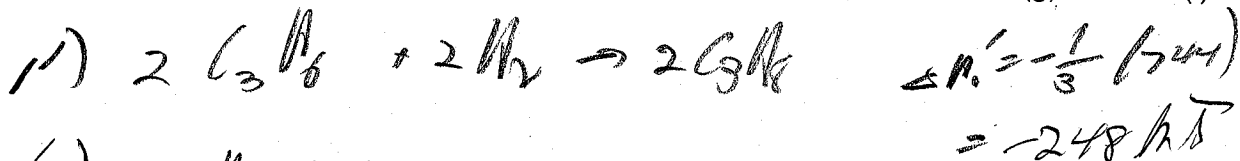
Div. num.
Denom. by V

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p}{-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa_T}$$

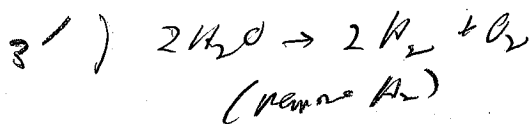
(14) 2. From the following enthalpies of reaction,



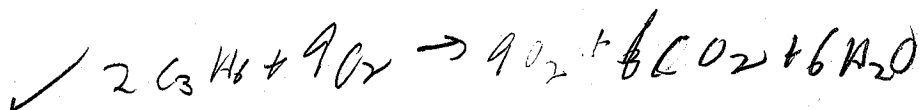
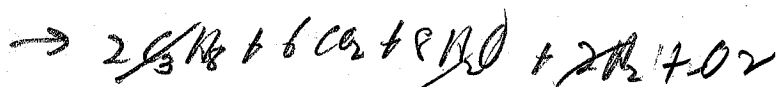
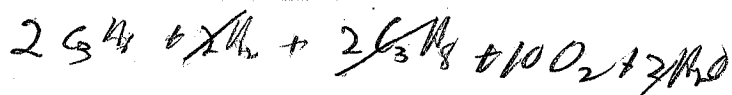
Calculate ΔH° for the reaction, $2 \text{C}_3\text{H}_6(\text{g}) + 9 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$



$\Delta H'_2 = -2(2220 \text{ kJ})$
 $= -4440 \text{ kJ}$



$\Delta H'_3 = -1(-572)$
 $= +572 \text{ kJ}$



$\Delta H = \Delta H'_1 + \Delta H'_2 + \Delta H'_3$
 $= -248 + (-4440) + 572$
 $= -4116 \text{ kJ}$

$$n = 2 \text{ mol} \\ T_1 = 300 \text{ K} \rightarrow p_1 = \frac{nRT_1}{V_1} = \frac{2(8.31)(300)}{20} = 249.3 \text{ kPa} \\ V_1 = 20 \text{ L}$$

(18) 2. A Perfect Gas has a temperature dependent molar constant pressure heat capacity, $C_{p,m} = a + bT^3$ with $a = 30 \text{ J/mol-K}$ and $b = 8 \times 10^{-8} \text{ J/(mol-K}^4\text{)}$.

Two (2) moles of this gas, originally at a temperature of 300 K and volume of 20. L is heated reversibly at **constant pressure** to a temperature of 800 K.

Calculate ΔH , ΔU , and w for this process (in kJ)

$$T_2 = 800 \text{ K} \rightarrow V_2 = \frac{nRT_2}{p_2} = \frac{2(8.31)(800)}{249.3} = 53.3 \text{ L}$$

$$\boxed{q = \Delta H} = \int_{T_1}^{T_2} n C_{p,m} dT = \int_{T_1}^{T_2} n (a + bT^3) dT = na \int_{T_1}^{T_2} dT + nb \int_{T_1}^{T_2} T^3 dT \\ = na [T_2 - T_1] + nb \left[\frac{T_2^4}{4} - \frac{T_1^4}{4} \right] \quad \leftarrow \text{Using } \int x^n dx = \frac{x^{n+1}}{n+1} \\ = 2 \text{ mol} (30 \text{ J/mol-K}) (800 \text{ K} - 300 \text{ K}) + 2 \text{ mol} (8 \times 10^{-8} \text{ J/mol-K}^4) \left[\frac{800^4}{4} - \frac{300^4}{4} \right] \\ = 3.00 \times 10^4 \text{ J} + 1.61 \times 10^5 \text{ J} \\ = 4.61 \times 10^4 \text{ J} = 46.1 \text{ kJ}$$

$$w = - \int_{V_1}^{V_2} p dV = -p [V_2 - V_1] = -249.3 \text{ kPa} [53.3 \text{ L} - 20 \text{ L}] \\ = -8.30 \times 10^3 \text{ kPa} \cdot \text{L} = -8.30 \times 10^3 \text{ J} = -8.30 \text{ kJ} = \boxed{-8.3 \text{ kJ}}$$

$$\Delta U = q + w = 46.1 \text{ kJ} - 8.3 \text{ kJ} = \boxed{37.8 \text{ kJ}}$$

or can integrate with $C_{p,m} = a' + bT^3$ [$a' = a - R$]

$$T = 218^\circ\text{C} \approx 491\text{K}$$

$$\Delta_{\text{cond}} H^\circ = -56\text{kJ/mol}$$

- (16) 3. The Enthalpy of Vaporization of Napthalene is 56.0kJ/mol and the normal boiling point is 218°C .

Calculation w , q , ΔU and ΔH (all in kJ) when four (4) moles of gaseous Napthalene are condensed to the liquid at 218°C and 1 atm pressure. $\text{Nap}(\text{gas}) \rightarrow \text{Nap}(\text{liq})$

Calc

$$q = \Delta H = n \Delta_{\text{cond}} H^\circ = 4\text{mol} (-56\text{kJ/mol})$$

$$= -224\text{kJ}$$

$$w = -P[V_{\text{liq}} - V_{\text{gas}}] = 0P V_{\text{gas}} = n_{\text{gas}} RT$$

$$= 4\text{mol} (8.31\frac{\text{J}}{\text{mol}\cdot\text{K}})(491\text{K})$$

$$= +16,300\text{J} \times \frac{1}{1000} = +16.3\text{kJ}$$

$$\Delta U = q + w = -224\text{kJ} + 16.3\text{kJ}$$

$$= -207.7 \approx -208\text{kJ}$$

(14) 5. Consider one mole of a gas which obeys the equation of state,

$$\left(p + \frac{A}{V^3}\right)V = RT \text{ with } A = 2.5 \text{ L}^3 \text{ atm} \rightarrow p + \frac{A}{V^3} = \frac{RT}{V} \rightarrow p = \frac{RT}{V} - \frac{A}{V^3}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} - 0$$

It can be shown that the dependence of internal energy on volume is:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Calculate the change in internal energy, ΔU (in in J) when one mole of this gas is expanded reversibly and isothermally from $V_1 = 0.50 \text{ L}$ to $V_2 = 0.90 \text{ L}$.

Notes: 1. $\Delta U \neq 0$ because this is NOT a Perfect Gas

2. $1 \text{ L-atm} = 101 \text{ J}$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\left(\frac{R}{V}\right) - \left[\frac{RT}{V} - \frac{A}{V^3}\right] = \frac{A}{V^3}$$

$$\Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \frac{A}{V^3} dV = A\left(-\frac{1}{2}\right)\left[\frac{1}{V^2}\right]_{V_1}^{V_2}$$

$$= -\frac{A}{2}\left[\frac{1}{V_2^2} - \frac{1}{V_1^2}\right] = -\frac{2.5 \text{ L}^3 \text{ atm}}{2}\left[\frac{1}{(0.90 \text{ L})^2} - \frac{1}{(0.50 \text{ L})^2}\right]$$

$$= +3.46 \text{ L-atm} \times \frac{101 \text{ J}}{1 \text{ L-atm}}$$

$$= +349 \approx \boxed{+350 \text{ J}}$$

$$\int \frac{1}{V^3} dV = \int V^{-3} dV = \frac{1}{-3+1} V^{-2} = -\frac{1}{2} \frac{1}{V^2}$$