INFORMATION PAGE (Use for reference and for scratch paper)

Constants and Conversion Factors:

R = 0.082 L-atm/mol-K = 8.31 J/mol-K = 8.31 kPa-L/mol-K

1 L-atm = 101 J

1 L-bar = 100 J

1 kPa-L = 1 J

1 bar = 100 kPa

1 bar = 750 torr

1 atm = 760 torr

1 atm = 1.013 bar = 1.013×10^5 Pa

Relations for Adiabatic Expansions and Compressions of a Perfect Gas

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} \quad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{C_{p,m}/C_{V,m}} = \left(\frac{V_1}{V_2}\right)^{\gamma} \qquad \gamma = \frac{C_{p,m}}{C_{V,m}}$$

Name___*Solutions*___

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

1. What are q and ΔU when 1.5 moles of a perfect gas is expanded reversibly and isothermally from 3.0 L to 20 L at 30 °C?

    (A) q = +7.2 kJ and $\Delta U = 0$

    (B) q = +7.2 kJ and ΔU = -7.2 kJ

    (C) q = 0 and ΔU = -7.2 kJ

    (D) q = -7.2 kJ and $\Delta U = 0$

2. The molar **constant volume** heat capacity of $O_2(g)$ is constant at $C_{V,m}$ = 24.5 J/mol-K. You can assume that $O_2(g)$ is a Perfect Gas. When 5. moles of $O_2(g)$ is heated **at constant pressure** from 100 °C to 300 °C,

    (A) ΔH = +24.5 kJ & w = +8.3 kJ

    (B) ΔH = +24.5 kJ & w = -8.3 kJ

    (C) ΔH = +32.8 kJ & w = -8.3 kJ

    (D) ΔH = +32.8 kJ & w = +8.3 kJ

3. For the reaction of one(1) mole of gaseous pentane, $C_5H_{12}(gas)$, with $O_2(gas)$ to form $CO_2(gas)$ and $H_2O(liq)$, at 75 °C, the internal energy change is ΔU = -3524 kJ. ΔH for this reaction at 75 °C is approximately.

    (A) -3512 kJ   (B) -3518 kJ   (C) -3530 kJ   (D) -3536 kJ

4. Consider the non-linear molecule, Ethylene ($CH_2=CH_2$) . What is the **constant pressure molar heat capacity, $C_{p,m}$,** of Ethylene, assuming that the molecules are free to translate   C, rotate and vibrate?

    (A) 15.0 R   (B) 15.5 R   (C) 16.0 R   (D) 16.5 R

5. Sodium metal reacts with hydrochloric acid according to the equation:

    $2\ Na(s) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + H_2(g)$.

    What is the work, w, when five(5) moles of Na(s) reacts with HCl(aq) at 25 °C and 1 atm. pressure?

    (A) -0.5 kJ   (B) -6.2 kJ   (C) -12.4 kJ   (D) +6.2 kJ

6. Consider the following Thermochemical equations:

    $$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g) \quad \Delta H = -196\ kJ$$
    $$4\ S(s) + 6\ O_2(g) \rightarrow 4\ SO_3(g) \quad \Delta H = -1580\ kJ$$

    Use these equations to determine ΔH for the reaction, $S(s) + O_2(g) \rightarrow SO_2(g)$.

    (A) -297 kJ   (B) -493 kJ   (C) -692 kJ   (D) +493 kJ

7. For the reaction $Fe_2O_3(s) + 3 CO(g) \rightarrow 2 Fe(s) + 3 CO_2(g)$, $\Delta H = -24$ kJ. The Enthalpy of Formations of $Fe_2O_3(s)$ and $CO_2(g)$ are -825 kJ/mol and -394 kJ/mol, respectively. Therefore, the enthalpy of formation of $CO(g)$ is

   (A) -111 kJ/mol   (B) -166.5 kJ/mol   (C) -127 kJ/mol

   (D) Cannot be determined without the Enthalpy of Formation of Fe(s)

8. The isothermal compressibility of a substance is defined by: $\pi_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T$

   Consider a hypothetical gas which follows the Equation of State: $p^2V = nRT$
   The isothermal compressibility of this hypothetical gas is given by:

   (A) $\dfrac{1}{T}$ (B) $\dfrac{1}{p}$ (C) $\dfrac{2V}{p}$ (D) $\dfrac{2}{p}$

9. The derivative, $\left(\dfrac{\partial U}{\partial p}\right)_T$, is a measure of the change in Internal Energy when the pressure is varied at constant temperature. For a gas in which **repulsive** interactions between molecules predominate, when the pressure on one mole of the gas is **decreased** isothermally from 5.bar to 1. bar then:

   (A) $\left(\dfrac{\partial U}{\partial p}\right)_T < 0$, $\Delta U < 0$ (B) $\left(\dfrac{\partial U}{\partial p}\right)_T < 0$, $\Delta U > 0$

   (C) $\left(\dfrac{\partial U}{\partial p}\right)_T > 0$, $\Delta U < 0$ (D) $\left(\dfrac{\partial U}{\partial p}\right)_T > 0$, $\Delta U > 0$

FIVE(5) PROBLEMS on following pages:

NOTE: You Must show your work to receive credit.

(12) 1. Starting with the differential form of the First Law, applied to a Perfect Gas:

$dU = dq + dw$ or $nC_{V,m}dT = dq - pdV$,

Prove that for a reversible adiabatic expansion (or compression) of a Perfect Gas,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}}.$$

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

$$nC_{V,m}dT = dq - pdV = 0 - \frac{nRT}{V}dV$$

$$\frac{dT}{T} = -\frac{R}{C_{V,m}}\frac{dV}{V}$$

$$\int_{T_1}^{T_2}\frac{dT}{T} = -\frac{R}{C_{V,m}}\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\ln\frac{T_2}{T_1} = -\frac{R}{C_{V,m}}\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{-R/C_{V,m}}$$

$$= \ln\left(\frac{V_1}{V_2}\right)^{+R/C_{V,m}}$$

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}}$$

(15) 2. Three (3) moles of a perfect gas, originally at a pressure of 80 kPa and volume of 100 L is compressed adiabatically and reversibly until the volume has decreased to 25 L. The constant volume molar heat capacity of the gas is $C_{V,m}$ = 26.5 J/mol-K

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

$q = 0$

$C_{V,m} = 26.5 \text{ J/K}$

$C_{p,m} = C_{V,m} + R = 26.5 + 8.31$

$\approx 34.8 \text{ J/K-K}$

$n = 3 \text{ mol}$
$P_i = 80 \text{ kPa}$
$V_1 = 100 \text{ L}, V_2 = 25 \text{ L}$

$T_1 = \dfrac{P_1 V_1}{nR}$

$= \dfrac{80 \times 100}{3 \times 8.31}$

$= 321 K$

$\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{R/C_{V,m}} = \left(\dfrac{100}{25}\right)^{8.31/26.5} = 1.545$

$T_2 = (321 K)(1.545) = 496 K$

$\Delta U = n\, C_{V,m} \Delta T = 3 \text{mol} (26.5 \frac{J}{mol\,K})(496 - 321)$
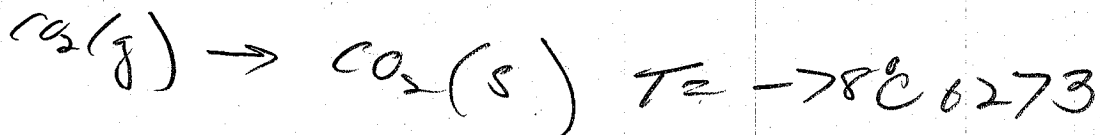
$= 13,910 J \times \dfrac{1}{1000} = \boxed{13.9 \text{ kJ}}$

$w = \Delta U - q = \Delta U - 0 = \boxed{13.9 \text{ kJ}}$

$\Delta H = n\, C_{p,m} \Delta T = 3 (34.8)(496 - 321)$

$= 18,270 J \times \dfrac{1}{1000} = \boxed{18.3 \text{ kJ}}$

(14) 3. Solid Carbon Dioxide (CO_2) sublimes directly to the gas at -78 °C. The Enthalpy of Sublimation of CO_2 is 25.2 kJ/mol.

Calculation w, q, and ΔU (all in kJ) when five(5) moles of gaseous CO_2 is converted to the solid (i.e. deposited) at -78 °C and 1 bar pressure.

$$CO_2(g) \rightarrow CO_2(s) \quad T = -78°C + 273$$
$$= 195 K$$

$$\Delta_{dep} H° = -\Delta_{sub} H°$$
$$= -25.2 \, kJ/mol$$

(const. P) $q = \Delta H = n \Delta_{dep} H° = 5 \, mol (-25.2 \, kJ/mol)$

$$= \boxed{-126.0 \, kJ}$$

$$W = -P \Delta V = -P[V_s - V_g] = +P V_g$$
$$= +nRT = 5 \, mol (8.314 \, J/(mol \cdot K))(195 K)$$
$$= +8100 \, J \times \frac{1}{1000} = \boxed{+8.1 \, kJ}$$

$$\Delta U = q + W = -126.0 + 8.1 = \boxed{-117.9 \, kJ}$$

$$\left(or \quad \Delta U = \Delta H - \Delta(PV) - gives \; same \; result \right)$$

$T_1 = 900K \quad n = 1.5 \, ml$

$T_2 = 300K$

(18) 4. A Perfect Gas has a temperature dependent **constant volume** molar heat capacity,

$C_{V,m} = a - \dfrac{b}{T^2}$, with a = 65. J/mol-K and b = 2.5x10⁶ J·K/mol.

1.5 moles of this gas, originally at a temperature of 900 K and volume of 50. L is cooled reversibly at **constant volume** to 300 K.

Calculate q, w, ΔU and ΔH for this process, in kJ.

$$\boxed{w = 0 \ (const. \ V)}$$

$$q = \Delta U = \int_{T_1}^{T_2} n \, C_{Vm} \, dT = \int_{T_1}^{T_2} n\left(a - \frac{b}{T^2}\right) dT$$

$$= na\int_{T_1}^{T_2} dT - nb \int_{T_1}^{T_2} \frac{1}{T^2} dT = na\left[T\right]_{T_1}^{T_2} - nb\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$= na\left[T_2 - T_1\right] + nb\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = 1.5 \, ml \left(65 \frac{J}{ml \cdot K}\right)(300K - 900K)$$

$$+ 1.5 \, ml \left(2.5\times10^6 \frac{J \cdot K}{ml}\right)\left[\frac{1}{300K} - \frac{1}{900K}\right]$$

$$= -58,500 \, J + 8330 \, J$$

$$= -50,170 \, J \approx \boxed{-50.2 \, kJ = q = \Delta U}$$

$$\Delta H = \Delta U + \Delta PV = \Delta U + (P_2 V_2 - P_1 V_1) = \Delta U + nRT_2 - nRT_1$$

$$= -50,170 \, J + 1.5 \, ml \left(8.31 \frac{J}{ml \cdot K}\right)(300K - 900K)$$

$$= -50,170 - 7480 \approx -57,640 \, J$$

$$\approx \boxed{-57.6 \, kJ}$$

$$\int \frac{1}{T^2} dT = \int T^{-2} dT$$

$$= \frac{1}{-2+1} T^{-2+1}$$

$$= -T^{-1} = -\frac{1}{T}$$

$$V - \frac{A}{p^2} = \frac{RT}{P} \Rightarrow V = \frac{RT}{P} + \frac{A}{p^2}$$

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

$$p\left(V - \frac{A}{p^2}\right) = RT \text{ with A = 25. L-atm}^2 \quad p_1 = 2\,atm$$

$$p_2 = 5\,atm$$

It can be shown that the dependence of enthalpy on pressure is given by:

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

Calculate the change in enthalpy, ΔH (in in kJ) when one mole of this gas is compressed reversibly and isothermally from p_1 = 2.0 atm. to p_2 = 5.0 atm. at 25 °C.

Notes: 1. ΔH ≠ 0 because this is NOT a Perfect Gas
       2. 1 L-atm = 101 J

$$\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial\left(\frac{RT}{P} + \frac{A}{p^2}\right)}{\partial T}\right)_p = \frac{R}{P} + 0$$

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{P} + \frac{A}{p^2} - T\left(\frac{R}{P}\right) = \frac{A}{p^2}$$

$$\Delta H = \int_{p_1}^{p_2}\left(\frac{\partial H}{\partial p}\right)_T dp = \int_{p_1}^{p_2} \frac{A}{p^2} dp = A\left[-\frac{1}{P}\right]_{p_1}^{p_2}$$

$$= +A\left[\frac{1}{P_1} - \frac{1}{P_2}\right] = 25\,L\cdot atm^2\left[\frac{1}{2\,atm} - \frac{1}{5\,atm}\right]$$

$$= 7.5\,L\cdot atm \times \frac{101\,J}{1\,L\cdot atm} = 758\,J \times \frac{1}{1000}$$

$$\approx \boxed{0.76\,kJ}$$