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

Trouton's Rule: $\Delta_{vap}S° = 85.$ J/mol-K

The relation between the Molar Mass (M), density (ρ) and Molar Volume (V_m) of a material is: $\rho = \dfrac{M}{V_m}$

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

For #1 - #2: Consider the reaction, $2 N_2O_5(g) \rightarrow 4 NO_2(g) + O_2(g)$. Relevant thermodynamic data is given in the table below:

Compound	S_m^o	$\Delta_f G^o$
$NO_2(g)$	240. J/mol-K	+51. kJ/mol
$O_2(g)$	205.	
$N_2O_5(g)$	356.	+115.

1. The Gibbs Energy Change ($\Delta_r G^o$) for the above reaction at 25 °C (in kJ) is approximately:

   (A) -128. kJ   (B) -26. kJ   (C) +26. kJ

   (D) Insufficient data is given

2. The standard Enthalpy Change ($\Delta_r H^o$) for the above reaction at 25 °C (in kJ) is approximately:

   (A) -161 kJ   (B) +109 kJ   (C) -109. kJ

   (D) Insufficient data is given

3. When two (2) moles of $N_2(g)$ at 25 °C and 50 L are compressed reversibly and isothermally to a final volume of 20 L, the entropy change is

   (A) -7.6 J/K   (B) +15.2 J/K   (C) -4.5 kJ/K   (D) -15.2 J/K

4. The **constant pressure** molar heat capacity of $CO_2(g)$ is 37.1 J/mol-K. What is ΔS when 5 moles of $CO_2(g)$ is heated at **constant volume** from 100 °C to 400 °C?

   (A) +25 J/K   (B) +109 J/K   (C) +85 J/K   (D) +300 J/K

5. A sample of 2 moles of $N_2(g)$ at 50 kPa and 20 L is compressed **reversibly** and **adiabatically** to a final pressure of 400 kPa. What is ΔS for this process?

   (A) +34.6 J/K   (B) 0 J/K   (C) -34.6 J/K   (D) -97.4 J/K

6. The normal boiling point of napthalene, $C_{10}H_8$, is 218 °C. An estimate of the Enthalpy of Vaporization of Napthalene using Trouton's Rule is:

   (A) 41.7 kJ/mol   (B) 52.1 kJ/mol   (C) 18.5 kJ/mol   (D) 28.9 kJ/mol

7. The normal boiling point of methanol is 64 °C. The Enthalpy of Vaporization of methanol is 35.3 kJ/mol. What is the entropy change of the **system** when **two (2)** moles of liquid methanol are vaporized reversibly to the gas at 64 °C?

(A) +210 J/K   (B) +105 J/K   (C) -105 J/K   (D) -210 J/K

8. The normal melting point of mercury is -39 °C. The enthalpy of fusion of mercury is 2.3 kJ/mol. What is the entropy change of the **surroundings** when **4 (four)** moles of liquid mercury are crystallized to the solid reversibly at -39 °C?

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

9. The change in the Gibbs energy (**in kJ**) when the volume of **2.5 moles** of ethane gas [$C_2H_6(g)$] is increased from isothermally 0.50 Liters to 10 Liters at 300 °C is:

(A) +35.7 kJ   (B) +14.3 kJ   (C) -35.7 kJ   (D) -18.7 kJ

10. The density of liquid toluene, C_7H_8(l) [M=92], is 0.90 g/mL at 50 °C. Therefore, the change in the Gibbs energy [in J] of **one(1)** mole of liquid toluene when the pressure is **increased** isothermally from 100 kPa to 5,000 kPa at 50 °C is approximately

(A) 1.6×10^3 J   (B) 5.0×10^2 J   (C) 1.1×10^4 J   (D) 5.0×10^5 J

11. A solid has two crystalline forms, A(s) and B(s). For the transition A(s) → B(s), $\Delta G° = -9.0$ kJ/mol (i.e. at 1 bar pressure). The difference in molar volumes of the two forms is $V_m(B) - V_m(A) = \Delta V_m = +2.0 \times 10^{-2}$ L/mol. This transition will be **spontaneous** at pressures _____ a pressure of _____ bar.

(A) above , 4.5×10^5 bar   (B) above , 4500 bar

(C) below , 4500 bar   (D) Spontaneous at all pressures

There are Four more MC questions on the following page

MULTIPLE CHOICE QUESTIONS (Continued)

For #12 - #15, consider the
phase diagram to the right
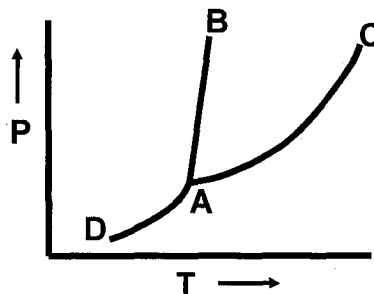
12. The Critical Point of the substance is represented by:

   (A) Point A   (B) Point B   (C) Point C   (D) Point D

13. The slope of curve A-D is **greater** than the slope of curve A-C because

   (A) $\Delta_{sub}V > \Delta_{vap}V$ (B) $\Delta_{vap}S > \Delta_{sub}S$

   (C) $\Delta_{sub}S > \Delta_{vap}S$ (D) $\Delta_{sub}V < \Delta_{vap}V$

14. The slope of curve A-B is **much greater** than the slope of curve A-C because

   (A) $\Delta_{fus}V < 0$ (B) $\Delta_{fus}V << \Delta_{vap}V$

   (C) $\Delta_{fus}S << \Delta_{vap}S$ (D) $\Delta_{fus}S >> \Delta_{vap}S$

15. If the pressure on this substance is **decreased** from 2000. bar to 1. bar, the melting
    point temperature will _____ and the boiling point temperature will _____

   (A) Decrease, Decrease   (B) Increase, Decrease
   (C) Decrease, Increase   (D) Increase, Increase

Four (4) Problems on following pages.

$T_1 = 250°C = 523 K$ $T_2 = 600°C = 873 K$

$n = 2 \text{ mol}$

(12) 1. A Perfect Gas has a temperature dependent molar constant pressure heat capacity, $C_{p,m} = a + bT^3$ with a = 30 J/mol-K and b = 8x10⁻⁸ J/(mol-K⁴).

Two (2) moles of this gas, originally at a temperature, of 250 °C and volume of 30. L is heated reversibly at **constant pressure** to a temperature of 600 °C.

Calculate the Entropy change, ΔS, for this process (in J/K)

$$\Delta S = \int_{T_1}^{T_2} \frac{n C_{p,m}}{T} dT = \int_{T_1}^{T_2} \frac{n(a + bT^3)}{T} dT$$

$$= na \int_{T_1}^{T_2} \frac{dT}{T} + nb \int_{T_1}^{T_2} T^2 dT$$

$$\boxed{\text{Used:} \quad \int x^2 dx = \frac{1}{3}x^3}$$

$$= na \ln\left(\frac{T_2}{T_1}\right) + \frac{nb}{3}\left[T_2^3 - T_1^3\right]$$

$$= 2 \text{ mol} (30 \text{ J/mol·K}) \ln\left(\frac{873}{523}\right) + \frac{2 \text{ mol}(8 \times 10^{-8} \frac{J}{mol·K^4})}{3}\left((873 K)^3 - (523 K)^3\right)$$

$$= 30.74 \text{ J/K} + 27.86 \text{ J/K}$$

$$= \boxed{+58.6 \text{ J/K}}$$

(15) 2. Consider a hypothetical gas that obeys the equation of state:

$$p(V - Ap) = nRT \implies V - Ap = \frac{nRT}{p} \implies V = \frac{nRT}{p} + Ap$$

If this gas undergoes an isothermal compression from p_1 to p_2, develop **INTEGRATED** expressions for ΔU, ΔH and ΔA in terms of n, R, T, A, p_1 and p_2.

$$\left(\frac{\partial V}{\partial T}\right) = \frac{nR}{p} \qquad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2} + A$$

From $dG = -SdT + Vdp \implies \left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p = -\frac{nR}{p}$

$dH = TdS + Vdp \implies \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = T\left[-\frac{nR}{p}\right] + \frac{nRT}{p} + Ap$

$$= Ap$$

$\therefore \Delta H = \int_{p_1}^{p_2}\left(\frac{\partial H}{\partial p}\right)_T dp = \int_{p_1}^{p_2} Ap\, dp \qquad \boxed{\frac{A}{2}\left[p_2^2 - p_1^2\right]} = \Delta H$

$dU = TdS - pdV \implies \left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T = T\left[-\frac{nR}{p}\right] - p\left[-\frac{nRT}{p^2} + A\right]$

$$= -Ap$$

$\Delta U = \int_{p_1}^{p_2}\left(\frac{\partial U}{\partial p}\right)_T dp = \int_{p_1}^{p_2} Ap\, dp \qquad \boxed{= \frac{A}{2}\left[p_2^2 - p_1^2\right]} = \Delta U$

$dA = -SdT - pdV \implies \left(\frac{\partial A}{\partial p}\right)_V = 0 - p\left(\frac{\partial V}{\partial p}\right)_T$

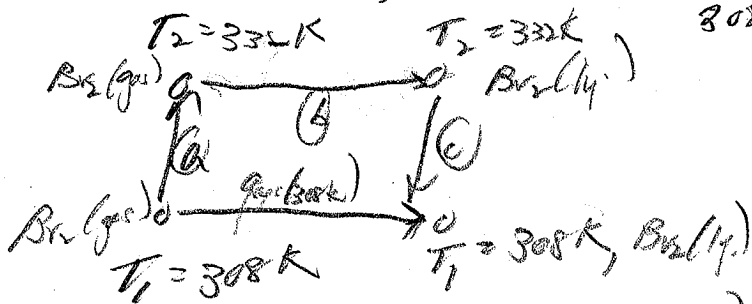$$= -p\left[-\frac{nRT}{p^2} + A\right] = +\frac{nRT}{p} - Ap$$

$\Delta A = \int_{p_1}^{p_2}\left[\frac{nRT}{p} - Ap\right] dp$

$$= \boxed{nRT \ln\left(\frac{p_2}{p_1}\right) - \frac{A}{2}\left[p_2^2 - p_1^2\right]} = \Delta A$$

(16) 3. The normal boiling point of Bromine liquid, Br_2(liq) is 59 °C.
The Enthalpy of Vaporization is 29.5 kJ/mol at 59 °C.
The constant pressure molar heat capacity of bromine liquid, Br_2(liq) is 76. J/mol-K
The constant pressure molar heat capacity of bromine gas, Br_2(gas), is 36. J/mol-K.

Calculate the entropy change of the **Surroundings**, ΔS_{surr} , (in J/mol-K) when
one (1) mole of supercooled Br_2(gas) condenses to Br_2(liq) at 30 °C.   35°C

To Calc ΔS_{surr}, we need. $\Delta S_{surr} = \dfrac{q_{surr}}{T} = -\dfrac{q_{sys}}{T}$ We need q_{sys}.

$\dfrac{}{308}$ $\dfrac{}{308}$ at 308 K.

$T_2 = 332K$ $T_2 = 332K$
$Br_2(gas)$ ———(b)———→ $Br_2(liq)$

(a)   (c)

$Br_2(gas)$ ———$q_{c}(308K)$———→ $Br_2(liq)$
$T_1 = 308K$ $T_1 = 308K$, $Br_2(liq)$

$\boxed{\Delta_{vap}H°(332K) = -\Delta_{vap}H°(308K)}$
$= -29.5 \, kJ$
$= -2.95 \times 10^4 \, J$

$q_{sys}(308K) = q_a + q_b + q_c = q_{heat} + q_{cond} + q_{cool}(liq)$

$= C_{p,m}(g)[T_2 - T_1] + \Delta_{vap}H°(332K) + C_{p,m}(liq)[T_1 - T_2]$

$= 36 \, J/K[332-308] + (-2.95 \times 10^4 J) + 76 \, J/K[308-332]$

$= +864 \, J + [-29,500 \, J] + [-1824 \, J]$

$q_{sys}(308K) = -30,460 \, J$

$q_{surr}(308K) = +30,460 \, J$

$\Delta S_{surr} = \dfrac{q_{surr}}{T} = \dfrac{+30,460 \, J}{308 \, K} = \boxed{+98.9 \, J/mol \cdot K}$

(12) 4 The densities of solid and liquid copper [Cu, M = 63.5] are 8.9 g/mL and 8.0 g/mL, respectively. The normal melting point of copper is 1085 °C. The enthalpy of fusion of copper is 13.3 kJ/mol.

What pressure must be applied (in bar) to increase melting point of Cu to 1100 °C?

$T_1 = 1085\,°C + 273 = 1358K$, $T_2 = 1100\,°C + 273 = 1373K$

$\Delta T = 15K = 15\,°C$

$\Delta_{fus}H^° = 1.33 \times 10^4\,J/mol \times \dfrac{1\,L\text{-}bar}{100J} = 133\ L\text{-}bar/mol$

$\Delta V_m = V_m(liq) - V_m(sol) = \dfrac{M}{d_{liq}} - \dfrac{M}{d_{sol}}$

$= \dfrac{63.5\,g/mol}{8.0\,g/cm^3} - \dfrac{63.5\,g/mol}{8.9\,g/cm^3} = 0.80\ cm^3/mol \times \dfrac{1L}{1000\,cm^3}$

$= 8.0 \times 10^{-4}\ L/mol$

$\dfrac{\Delta P}{\Delta T} = \dfrac{\Delta_{fus}H^°}{T\,\Delta V_m} = \dfrac{133\,L\text{-}bar/mol}{(1358K)(8.0 \times 10^{-4}\,L/mol)} = 122\ bar/K$

$\Delta p = 122\ bar/K \times 15K = \boxed{1830\ bar.}$