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: $\rho = \dfrac{M}{V_m}$

NOTE: if a question asks for the value of ΔS (without stating it's the "surroundings"), it is asking for the value of ΔS for the system.

Name_____Solutions_____

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

1. The entropy change is +237 J/K for the reaction: $2\,HgO(s) \rightarrow 2\,Hg(l) + O_2(g)$. The standard molar entropies of $HgO(s)$ and $O_2(g)$ are 70 J/mol-K and 205 J/mol-K. Therefore, the standard molar entropy of $Hg(l)$ is:

   (A) 86 J/mol-K   (B) 0 J/mol-K   (C) 51 J/mol-K   (D) 102 J/K

   For #2: Consider the reaction, $2\,SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g)$. Relevant thermodynamic data is given in the table below:

Compound	S_m°	$\Delta_f G^\circ$
$SO_2(g)$	248 J/mol-K	-350 kJ/mol
$O_2(g)$	205	
$SO_3(g)$	257	-371

2. The Enthalpy change (ΔH°) change for the above reaction at 25 °C is:

   (A) +13.7 kJ   (B) -46.7 kJ   (C) -97.7 kJ

   (D) There is insufficient data

3. A sample of 0.5 moles of $O_2(g)$ originally at 500 kPa and 5 L is expanded reversibly and isothermally to a final pressure of 100 kPa. What is ΔS for this process?

   (A) +13.4 J/K   (B) -6.7 J/K   (C) +4030 J/K   (D) +6.7 J/K

4. The **constant volume** molar heat capacity of Ar(g) is 12.5 J/mol-K. What is ΔS when 3 moles of Ar(g) is cooled at **constant pressure** from 500 °C to 100 °C?

   (A) +27.3 J/K   (B) -45.5 J/K   (C) -100.5 J/K   (D) -27.3 J/K

5. A sample of 3 moles of $O_2(g)$ at an initial temperature of 100 °C and initial volume of 60 L is expanded **reversibly** and **adiabatically** to a final volume of 200 L. What is ΔS for this process?

   (A) -30 J/K   (B) +11.2 kJ/K   (C) 0 kJ/K   (D) +30 J/K

For #6 - #8: The normal boiling point of methanol [CH_3OH, M=32] is 65 °C. The Enthalpy of Vaporization of methanol is 35.2 kJ/mol.
80 grams of methanol gas are condensed to the liquid at 65 °C and 1 bar pressure. Calculate the following quantities for this condensation:

6. The Entropy Change, ΔS, for this process is approximately

   (A) +260 J/K   (B) -104 J/K   (C) -260 J/K

   (D) None of the above

7. The work, w, for this process is approximately

   (A) +7.0 kJ   (B) +8.8 kJ   (C) -7.0 kJ

   (D) None of the above

8. The Internal Energy change, ΔU for this process is approximately

   (A) -95 kJ   (B) -81 kJ   (C) -88 kJ

   (D) None of the above

9. The normal boiling point of toluene is 111 °C. The enthalpy of vaporization of toluene is 39.2 kJ/mol. What is the entropy change of the **surroundings** when one mole of toluene vaporizes at 111 °C?

   (A) +102 J/mol-K   (B) +35.3 J/mol-K   (C) -102 J/mol-K   (D) -353 J/mol-K

10. The Enthalpy of Vaporizaton of cyclooctane, C_8H_{16}, is 37.0 kJ/mol. An estimate of the normal boiling point **(in °C)** of cyclooctane using Trouton's Rule is:

    (A) 128 °C   (B) 435 °C   (C) 294 °C   (D) 162 °C

11. The change in the Gibbs Energy for a certain constant pressure process is given by:
    $\Delta G = a + bT^2$, a = 4,000 J , b = 5. x10⁻² J/K². The value of ΔS for this process at 50 °C is approximately:

    (A) -16 J/K   (B) -32 J/K   (C) 0 J/K   (D) +32 J/K

12. The density of liquid benzene,, C_6H_6(l) [M=78], is 0.85 g/mL at 50 °C. Therefore, the change in the Gibbs energy [in J] of **one(1)** mole of benzene when the pressure is **increased** isothermally from 100 kPa to 10,000 kPa at 50 °C is approximately

    (A) 910 J   (B) 9.1x10⁴ J   (C) 1.2x10⁴ J   (D) 770 J

There are Five more MC questions on the following page

13. A solid has two crystalline forms, A(s) and B(s). For the transition A(s) → B(s), ΔG° = +10. kJ/mol (i.e. at 1 bar pressure). The difference in molar volumes of the two forms is $V_m(B) - V_m(A) = \Delta V_m = -25.$ mL/mol. This transition will be **spontaneous** at pressures _____ a pressure of _____ bar.

(A) above , 4×10^5 bar

(B) below , 4000 bar

(C) above , 4000 bar

(D) Not spontaneous at any pressure

For #14 - #17, consider the phase diagram on the right.
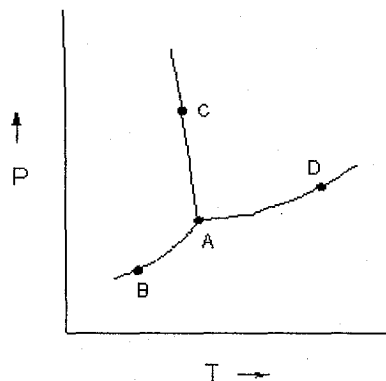
14. The Triple Point in the diagram is represented by

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

15. The slope of curve A-B is steeper than the slope of curve A-D because

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

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

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

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

16. The slope of curve A-C is negative because

(A) $\Delta_{fus}S^\circ > 0$

(B) $\Delta_{fus}S^\circ < 0$

(C) $V_m(liq) > V_m(sol)$

(D) $V_m(sol) > V_m(liq)$

17. If the pressure on this substance is increased from 1 bar to 500 bar, the boiling point will _____ and the melting point will _____.

(A) decrease, increase

(B) increase, increase

(C) increase, decrease

(D) increase/ increase or decrease depends on relative solid and liquid entropies

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There are Three (3) Problems on following pages.

(18) 1. A Perfect Gas has a temperature dependent **constant pressure** molar heat capacity, $C_{p,m} = a - \dfrac{b}{T^2}$, with a = 75. J/mol-K and b = 3.0x10⁶ J•K/mol.

3 moles of this gas, originally at a temperature of 100 °C and volume of 75. L is heated reversibly at **constant pressure** to 400 °C.

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

$$\Delta S = \int_{T_1}^{T_2} \frac{n\, C_{p,m}\, dT}{T} = \int_{T_1}^{T_2} \frac{n\left(a - b/T^2\right) dT}{T}$$

$$= na\int_{T_1}^{T_2} \frac{dT}{T} - nb\int_{T_1}^{T_2} \frac{dT}{T^3}$$

$$= na\,\ln\!\left(\frac{T_2}{T_1}\right) - (nb)\left(-\frac{1}{2}\right)\left[\frac{1}{T_2^2} - \frac{1}{T_1^2}\right]$$

$$= 3(75)\,\ln\!\left(\frac{673}{373}\right) + \frac{3(3\times10^6)}{2}\left[\frac{1}{(673)^2} - \frac{1}{(373)^2}\right]$$

$$= +132.8\,\frac{J}{K} + \left(-26.9\,\frac{J}{K}\right)$$

$$= +105.9\,\frac{J}{K} = \boxed{+106\,\frac{J}{K}}$$

$n = 3\,mol$
$T_1 = 100\,°C = 373K$
$T_2 = 400\,°C = 673K$

$$\int_{T_1}^{T_2}\frac{dT}{T^3} = \int_{T_1}^{T_2} T^{-3}\,dT$$

$$= \frac{1}{-3+1}\left[T^{-3+1}\right]_{T_1}^{T_2}$$

$$= -\frac{1}{2}\left[\frac{1}{T_2^2} - \frac{1}{T_1^2}\right]$$

Part (b) is on following page

$$T_1 = 373$$
$$\overline{T_2} = 673$$

(18) 1. **CONT'D**

A Perfect Gas has a temperature dependent **constant pressure** molar heat

capacity, $C_{p,m} = a - \dfrac{b}{T^2}$, with a = 75. J/mol-K and b = 3.0x10^6 J•K/mol.

3 moles of this gas, originally at a temperature of 100 °C and volume of 75. L is
heated reversibly at **constant pressure** to 400 °C.

(9) (b) Calculate the heat (q) and work (w) for this process (in kJ).

$$\boxed{q} \quad q = \Delta H = \int_{T_1}^{T_2} n C_{p,m}\, dT = \int_{T_1}^{T_2} n\left(a - \frac{b}{T^2}\right) dT$$

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

$$= 3(75)(673 - 373) - 3(3\times10^6)\left(\frac{1}{373} - \frac{1}{673}\right)$$

$$= + 67,500\ J - 10,766\ J = 56,740\ J = \boxed{56.7\ kJ}$$

$$\boxed{w} \quad Const\ P$$

$$w = -P(V_2 - V_1) = -PV_2 + PV_1$$

$$= -nRT_2 + nRT_1 = nR(T_1 - T_2)$$

$$= 3(8.31)(373 - 673)$$

$$= -7480\ J = \boxed{-7.5\ kJ}$$

(16) 2. The normal melting point of CHCl₃ is -63 °C.
The Enthalpy of Fusion of CHCl₂ at -63 °C is 8.80 kJ/mol
The constant pressure heat capacity of liquid CHCl₃ is 116 J/mol-K
The constant pressure heat capacity of solid CHCl₃ is 96 J/mol-K

Calculate the entropy change of the **system**, ΔS_{sys}, when one (1) mole of liquid trichloromethane freezes irreversibly to the solid at -90 °C.

$T_1 = -90°C = 183K$

$T_2 = -63°C = 210K$

$C_p(liq) = 116\ J/mol\text{-}K$

$C_p(sol) = 96\ J/mol\text{-}K$

$\Delta H_{fus}^{o}(210K) = +8.8\ kJ/$

$\Delta H_{fus}^{o}(210K) = -8.8\ kJ/$

$= -8.8 \times 10^3\ J/$

$T_2 = 210K$ $S = 210K,\ sol.$

ΔS_1 ΔS_2

ΔS_3

$T_1 = 183$ $T_1 = 183K,\ sol.$
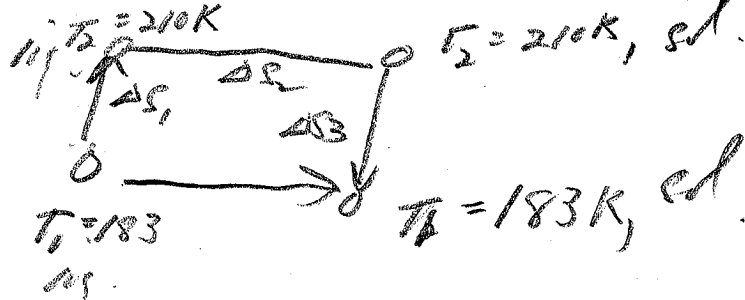
$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$= C_p(liq)\ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{fus}^{o}}{T_2} + C_p(sol)\ln\left(\frac{T_1}{T_2}\right)$

$= 116\ J/mol\cdot K\ \ln\left(\frac{210}{183}\right) + \frac{-8.8 \times 10^3\ J}{210K} + 96\ \ln\left(\frac{183}{210}\right)$

$\Delta S = +15.96\ J/mol\cdot K + (-41.90\ J/mol\cdot K) + (-13.21\ J/mol\cdot K)$

$= -39.15 \approx \boxed{-39.2\ J/mol\cdot K}$

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

$$(p + BV^2)V = RT, \text{ where B is a constant}$$

If this gas undergoes an isothermal expansion from V_1 to V_2, develop **INTEGRATED** expressions for ΔU, ΔH and ΔG in terms of B, R, T, V_1 and V_2.

$$P = \frac{RT}{V} - BV^2 \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} - 2BV$$

From $dA = -SdT - pdV \longrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$

$\boxed{\Delta U}$

$$dU = TdS - pdV \longrightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{R}{V}\right) - \left[\frac{RT}{V} - BV^2\right]$$

$$= + BV^2$$

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

$\boxed{\Delta H}$

$$dH = TdS + Vdp \longrightarrow \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

$$= T\left(\frac{R}{V}\right) + V\left(-\frac{RT}{V^2} - 2BV\right) = -2BV^2$$

$$\Delta H = \int_{V_1}^{V_2} -2BV^2 \, dV = \boxed{-\frac{2B}{3}\left[V_2^3 - V_1^3\right]}$$

$\boxed{\Delta G}$

$$dG = -SdT + Vdp \longrightarrow \left(\frac{\partial G}{\partial V}\right)_T = 0 + V\left(\frac{\partial P}{\partial V}\right)_T = V\left[-\frac{RT}{V^2} - 2BV\right]$$

$$= -\frac{RT}{V} - 2BV^2$$

$$\Delta G = \int_{V_1}^{V_2} -\frac{RT}{V} \, dV + \int_{V_1}^{V_2} -2BV^2 \, dV$$

$$= \boxed{-RT\ln\left(\frac{V_2}{V_1}\right) - \frac{2B}{3}\left[V_2^3 - V_1^3\right]}$$