1. Find the melting point of ice at 100 atm if $\Delta H_{\text{fusion}} = 79.7 \text{ cal gm}^{-1}$.

$\rho = 0.917 \text{ gm cm}^{-3}$ for ice at $0^0 \text{ C}$ and 1 atm and

$\rho = 1.00 \text{ gm cm}^{-3}$ for water at 1 atm. (Ans : 272.4 K)

$\Delta H_{\text{fusion}} = 79.7 \text{ cal gm}^{-1}$

$\Delta V_{\text{fusion}} = V_{\text{liq}} - V_{\text{solid}}$

$= -0.091 \text{ cm}^3$

$\ln \frac{T_2}{T_1} = \left(\frac{P_2 - P_1}{P_1}\right) \frac{\Delta V_{\text{fusion}}}{\Delta H_{\text{fusion}}}$

After substitution, $T_2 \approx 272.4 \text{ K.}$
2. What is the change in the boiling point of H$_2$O at 100$^\circ$C per m.m change in the atmospheric pressure? The heat of vapourisation is 539.7 cal gm$^{-1}$. The molar volume of H$_2$O (l) is 18.78 ml and that of H$_2$O (g) is 30.199 lit. (at 100$^\circ$C and 1 atm )

(Ans : $dP/dT = 0.037$ K mm$^{-1}$)

\[
\frac{dP}{dT} = \frac{\Delta H_{vap}}{T C (V_v - V_l)} = 27.1 \text{ mm Hg K}^{-1}.
\]

$\therefore \frac{dT}{dP} = 0.037$ K mm Hg$^{-1}$
3. The internal energy change ($\Delta U$) for the combustion of ZrC(s) was $-310863$ cal/mol at $25^0\text{C}$. Calculate the enthalpy of combustion for (Ans : $-311.5$ K cal mol$^{-1}$)

$$\Delta H = \Delta U + (\Delta n) RT$$
$$\Delta U = \Delta H - (\Delta n) RT$$
$$= -310863 - (-1) \times 2 \times 298$$
$$\simeq -310.2 \text{ K cal mol}^{-1}.$$
4. Nitrobenzene was steam distilled at 98.7° C when the atmospheric pressure was 99.56 KPa. Calculate the % composition by the mass of the distillate given that the vapour pressure of H₂O and nitrobenzene are 96.63 and 2.93 kPa respectively.

(Ans: 17.2 % Nitrobenzene)

\[
p_w/p_e = \frac{W_w}{M_w} / \frac{W_e}{M_e}
\]

Consider 100 gms of the distillate.
Let x be the weight of nitrobenzene.
\[
x /100 - x = 2.93 x 123/96.63 x 18
\]
\[
\therefore x = 17.2
\]
17.2 wt % Nitrobenzene
5. The normal boiling point of C₆H₆ at 1 atm pressure is 353.2 K. Estimate the pressure at which C₆H₆ would boil at 330 K. (Ans : 0.47 atm)

To obtain $\Delta H_v$, employ Trouton’s rule ($\Delta S_v = 88$ J/K is the normal value)

$\therefore \Delta H_v \approx 31800$ J/mol

$\ln \frac{P_2}{P_1} = \frac{31800 \times (330 - 353.2)}{(8.314) (353.2) (300)}$

$\therefore P_2 \approx 0.432$ atm.

Note: Depending upon the value of $\Delta H_v$ employed, the answer for $P_2$ may vary slightly.
6. Evaluate $\Delta G^0$, $\Delta H^0$, and $\Delta S^0$ at 298 K for the reaction SOCl$_2$(l) + H$_2$O(l) $\rightarrow$ SO$_2$(g) + 2HCl(g) from the following data

<table>
<thead>
<tr>
<th>Quantity</th>
<th>SOCl$_2$(l)</th>
<th>H$_2$O(l)</th>
<th>SO$_2$(g)</th>
<th>HCl(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^0_{298}$ (J mol$^{-1}$K$^{-1}$)</td>
<td>215.7</td>
<td>69.9</td>
<td>248.1</td>
<td>186.8</td>
</tr>
<tr>
<td>$\Delta H^0_{298}$ (KJ mol$^{-1}$)</td>
<td>-245.6</td>
<td>-241.8</td>
<td>-296.8</td>
<td>-92.3</td>
</tr>
</tbody>
</table>

(Ans: $\Delta S^0_{298} = 336.1$ J mol$^{-1}$ K$^{-1}$; $\Delta H^0_{298} = 49.4$ KJ mol$^{-1}$; $\Delta G^0_{298} = -50.8$ KJ / mol)

$\Delta G^0$, $\Delta H^0$, $\Delta S^0$ for the reaction

$\Delta H^0_{298} = [ - (296.8) + 2 (-92.3)] - [-245.6 - 241.8]$

$= 6$ kJ / mol.

$\Delta S^0_{298} = 336.1$ Jk$^{-1}$ mol$^{-1}$; $\Delta G^0_{298} = 6000 - (298) (336.1) = -94.15$ kJ
7. Calculate the change in the free energy of 1 mole of acetylene when it is heated from 500K to 600 K at constant pressure. The average entropy of acetylene in this temperature change is 230 J/K/mol

\[ dG = VdP - SdT \]
\[ \Delta G = -S(T_2 - T_1) \]
\[ = -230 \times (600 - 500) = -2300 \text{ J/mol}. \]

(Ans : 23KJ/mol).
8. From the given data predict whether the reaction \( \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH} \ (\text{l}) \) is spontaneous.

\[
\begin{array}{c|cc}
\text{Comp} & \Delta H^0 \ (\text{KJ/mol}) & S^0 \ (\text{J/K/mol}) \\
\hline
\text{C}_2\text{H}_5\text{OH} \ (\text{l}) & -277.69 & 160.7 \\
\text{H}_2\text{O} \ (\text{l}) & -285.83 & 69.91 \\
\text{C}_2\text{H}_4(\text{g}) & 52.26 & 291.56 \\
\end{array}
\]

(Ans: -5.75 KJ. Spontaneous)

\[
\Delta S^0 = 160.7 - (69.91 + 291.56) \\
= -200.77 \ \text{Jk}^{-1}\text{mol}^{-1}
\]

\[
\Delta H^0 = -277.69 - (-285.83 + 52.26) \\
= -44.12 \ \text{KJ mol}^{-1}
\]

\[
\Delta G^0 = -44120 - (298) (-200.77) \\
= 15.709 \ \text{J mol}^{-1}
\]

= +ve \therefore \text{non-spontaneous in the direction specific.}
9. The change in the Gibbs free energy values, under standard conditions, \((\Delta G^0)\) for a reaction at 500 K and 510 K are \(-122\) KJ and \(-124\) KJ respectively. Calculate the values of \(\Delta H\) and \(\Delta S\) assuming that they do not vary with the temperature.

\[
\text{(Ans : } \Delta H = -22\text{ KJ } \& \Delta S = -200\text{J/K})
\]

Ans: \(T_1 = 500\) K; \(T_2 = 510\) K.

\[
\begin{align*}
\Delta G^0_{T2} &= -124 \text{ kJ} \\
\Delta G^0_{T1} &= -122 \text{ kJ} \\
\Delta G^0_{T2}/T_2 - \Delta G^0_{T1}/T_1 &= \Delta H^0 \left[1/510 - 1/500\right] \\
-124/510 + 122/500 &= \Delta H^0(-10)/500 \times 510 \\
-0.2431 + .244 &= \Delta H^0 (-3.921 \times 10^{-5}) \\
\Delta H^0 &= 9 \times 10^{-4} / -3.921 \times 10^{-5} \\
\approx -90/3.92 &\approx -22.96 \text{ kJ.}
\end{align*}
\]

\[
\therefore \Delta G^0_{500\text{K}} = -22.96 - (500) \text{ kJ}
\]

\[
\therefore \Delta S^0 \text{ at } 500\text{ K} \approx 0.198 \text{ kJ}
\]
10. For an equilibrium process, a plot of ln K against 1/ T gave a straight line with a negative slope, equal to 7040 K\(^{-1}\). Find the value of \(\Delta H^0\). 

\[ \text{Ans: } \frac{d \ln K}{d \left(\frac{1}{T}\right)} = -\frac{\Delta H^0}{R} \]

\[ \therefore \Delta H^0 = 58.53 \text{ kJ mol}^{-1} \]
11. At 25°C the distribution ratio of H₂S between water and benzene is 0.17 (a) what is the minimum volume of benzene necessary at 25°C to extract in one step 90% of H₂S present in one litre of a 0.1 M aq. solution? b) using 100 cc of benzene every time, how many extractions will be required to complete 90% extraction?

(Ans : a = 1530 CC ; b = 5 extractions)

Ans: \( K = \frac{[H_2S]_{H_2O}}{[H_2S]_{C6H6}} = \frac{1}{5.88} \) i.e., 0.17

a) \( W_1 = 10 = 100 \left(\frac{0.17}{0.17} + y\right) \)
\( 100 \left(\frac{0.17}{0.17} + y\right) = 10 \)
\[ y = 1.53 \text{ litres for 90% extraction.} \]

b) For what value of \( n \),
\[ 10 = 100 \left(\frac{0.17}{0.17} + 0.1\right)^n \] is valid?
\[ n \approx 5 \]
\[ \therefore 5 \text{ extractions.} \]
12. When aniline (M.Wt= 93 gm mol⁻¹) is steam distilled at 1 atm, the distillate is found to contain 26.5 % by wt. of aniline. What is the vapour pressure of aniline at the temperature of distillation?

(Ans: 0.0652 atm / 49.57 mm.Hg)

Ans: \[
\frac{26.5}{73.5} = \frac{p_e}{760 - p_e} \frac{93}{(760 - p_e)} 18
\]
\[
p_e / 760 - p_e = 18 \times 26.5 / 93 \times 73.5 = 0.06978
\]
\[
\therefore p_e = 49.57 \text{ mm Hg}.
\]
13. Construct the phase diagram of a two component system forming simple eutectic. Apply the phase rule in each region. Draw the cooling cure for pure A, at eutectic composition and another one in between these two compositions.

Ans: Phase diagram of a two - component system forming a simple eutectic.
14. The equilibrium constant of the reaction
C (graphite ) + 2 H₂(g) = CH₄(g), at 35⁰C is 3.036 X 10⁸ and
ΔH° for the reaction in the temperature range 25 – 35⁰C is 179 K cal. Calculate ΔG° at 25⁰C

(Ans : - 5754 Cals )

K_p at 308 K = given
ΔG°₃₀₈ = - RT ln (3.036 x 10⁸)
= -2 x 308 x 19.5312 cal mol⁻¹.
= -12.031 K cal mol⁻¹

ΔG°₃₀₈ / 308 - ΔG°₂₉₈ / 298 = ΔH° (1/308 – 1/298)
-12.031/308 - ΔG°₂₉₈ / 298 = 179 (-10)/(298) (308)
∴ΔG°₂₉₈ ≃ -5.82 k. cal.
15. The vapour pressure in torr for ice and liq. water are given by the equations. (energy in joules)

\[
\ln P\text{ (ice)} = 24.00 - \frac{6140.1}{T} \\
\ln P\text{ (H}_2\text{O)} = 21.41 - \frac{5433}{T}
\]

Calculate the triple point temperature and pressure. Determine the molar enthalpies of vapourisation, sublimation and fusion of H\textsubscript{2}O at its triple point

(Ans: 273.01 K & 4.55 torr; 45.2, 51.1 & 5.9 Kj/mol)

Ans: At the triple point temperature,

\[
24.00 - \frac{6140.1}{T} = 21.41 - \frac{5433}{T}
\]

\[
\therefore \frac{6140.1}{T} - \frac{5433}{T} = 2.59
\]

\[
\frac{707.1}{T} = 2.59
\]

\[
\therefore T = 273.01 \text{ K}
\]

Substituting in any of the equations,
we obtain the triple point pressure as
\[ \ln P = 24.00 - \frac{6140.1}{273.01} \]
\[ = 1.509 \]
\[ \therefore P \approx 4.52 \text{ Torr}. \]

From the first eqn, \( \frac{d \ln p}{dT} = \frac{6140.1}{T^2} = \Delta H^0 \text{ (sublimation)}/RT^2 \)
\[ \therefore \Delta H^0_{\text{sub}} = 6140.1 \times 8.314 = 51.05 \text{ kJ/mol}^{-1}. \]
From the second eqn, \( \frac{d \ln p}{dT} = \frac{5433}{T^2} = \Delta H^0 \text{ (vap)}/RT^2 \)
\[ \therefore \Delta H^0_{\text{vap}} = 45.17 \text{ kJ/mol} \]
\[ \therefore \Delta H^0_{\text{fusion}} = 51.05 - 45.17 = 5.88 \text{ kJ/mol}^{-1}. \]
16. Calculate the change in entropy of a mole of aluminium (at.wt .27) which is heated from 600 to 700°C. The m.pt. of Al is 660°C, the heat of fusion is 393 Jg⁻¹ and the heat capacities of the solid and liquid may be taken as 31.8 amd 34.3 JK⁻¹ mol respectively.

(Ans: 14.92 JK⁻¹ mol⁻¹)

\[ \Delta S = C_p^s \ln \frac{T_m}{T_1} + \Delta H_f/T_m + C_p^l \ln \frac{T_2}{T_m} \]

\[ \Delta H_f = 393 \text{ J gm}^{-1} = 10.611 \text{ kJ mol}^{-1}. \]

\[ \therefore \Delta s = 31.8 \ln \frac{933}{873} + \frac{10611}{933} + 34.4 \ln \frac{973}{933} \approx 14.93 \text{ JK}^{-1} \text{ mol}^{-1}. \]
17. Based on the Trouton’s rule, calculate the molar heat of vapourisation of benzene at its boiling point of 353 K (Ans: 31 KJ)

\[ \Delta H^0 = 90 \text{ J mol}^{-1} \quad \therefore \Delta H^0_v = 90 \times 353 \approx 31.77 \text{ kJ} \]

18. Calculate the molar heat capacity of a non-linear triatomic gas assuming that the principle of equipartition is valid (Ans: 49.9 J mol\(^{-1}\) deg\(^{-1}\))

Ans: \[ C_v = \frac{3R}{2} + \frac{3R}{2} + 3R \approx 49.88 \text{ Jk}^{-1} \text{ mol}^{-1}. \]
19. For the reaction \( \text{CO}_2 \text{(g)} + \text{H}_2 \text{(g)} \rightleftharpoons \text{CO}_2 \text{(g)} + \text{H}_2\text{O} \text{(g)} \) \( K_p \) is 0.63 at 700\(^0\) C and 1.66 at 100\(^0\) C. a) What is the average value of \( K_p \) in this temperature range? b) What is the value of \( K_p \) at 800\(^0\)C?

(Ass : \( \Delta H = 8 \times 10^3\text{cal, } K_p = 0.93 \))

\[
\ln \frac{K_p(T_2)}{K_p(T_1)} = \frac{\Delta H^0(T_2 - T_1)}{R T_1 T_2}
\]

\( K_p(973 \text{ K}) = 0.63; \ K_p(373 \text{ K}) = 1.66 \)

\( \Delta H^0 = -1.17 \times 10^3 \text{ cal} \)

\[
\ln \frac{K_p(T_2 - 1073k)/0.63 = \Delta H^0/R (1073 - 973)/(1073 \times 973)}{0.63} = \Delta H^0/R (1073 - 973)/(1073 \times 973)
\]

\( \therefore K_p \) at 1073 K \( \approx 0.67 \)