Principal issues discussed:

Carnot engine
Definition of entropy
Entropy calculations – reversible, irreversible
Clausius inequality, conditions of equilibrium A, G
Gibbs free energy, G as a function of T
Variation of G, VdP-SdT
Free energy and chemical equilibrium
Maxwell’s relations
Phase equilibrium

Boltzmann distribution
Molecular partition function, U
Cannonical partition function
Translational partition function

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 \( 0^\circ \text{C} \) and 1 atm and \( \rho = 1.00 \text{ gm cm}^{-3} \) for water at 1 atm.

\[
\text{(Ans : 272.4 K)}
\]

Ans: \( \Delta H_{\text{fusion}} = 79.7 \text{ cal gm}^{-1} \)
\[
\Delta V_{\text{fusion}} = V_{\text{liq}} - V_{\text{solid}}
\]
\[
= -0.091 \text{ cm}^3
\]
\[
\ln \frac{T_2}{T_1} = (P_2 - P_1) \frac{\Delta V_{\text{fusion}}}{\Delta H_{\text{fusion}}}
\]
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 : \( \frac{dT}{dP} = .037 \text{ K mm}^{-1} \))

Ans: \( dP/dT = \Delta H_{\text{vap}}/T (V_v - V_l) \)
\[
= 27.1 \text{ mm Hg K}^{-1}.
\]
\[ \therefore \frac{dT}{dP} = 0.037 \text{ K mm Hg}^{-1} (\text{K/Torr}) \]

3. The internal energy change (\( \Delta U \)) for the combustion of ZrC(s) was \(-310863 \text{ cal/mol} \) at \( 25^\circ \text{C} \). Calculate the enthalpy of combustion for

\[ [\text{ZrC(s)} + 2\text{O}_2(g) \rightarrow \text{ZrO}_2(s) + \text{CO}_2(g)] \quad (\text{Ans : -310.2 K cal mol}^{-1}) \]

\( \Delta H = \Delta U + (\Delta n) \text{RT} \)

\[ = -310863 - (\text{-1}) \times 2 \times 298 \]

\( \approx -310.2 \text{ k cal mol}^{-1} \).

4. The normal boiling point of \( \text{C}_6\text{H}_6 \) at 1 atm pressure is 353.2 K. Estimate the pressure at which \( \text{C}_6\text{H}_6 \) would boil at 330 K. (Ans : 0.432 atm)

Ans: To obtain \( \Delta H_v \), employ Trouton’s rule

\[ \therefore \Delta H_v \approx 31800 \text{ J/mol} \]

\[ \ln \frac{P_2}{P_1} = 31800 \times (330 - 353.2) / (8.314) (353.2) (330) \]

\[ : P_2 \approx 0.432 \text{ atm.} \]

Note: Depending upon the value of \( \Delta H_v \) employed, the answer for \( P_2 \) may vary slightly.

5. Evaluate \( \Delta G^0, \Delta H^0, \text{ and } \Delta S^0 \) at 298 K for the reaction \( \text{SOCl}_2(l) + \text{H}_2\text{O(g)} \rightarrow \text{SO}_2(g) + 2\text{HCl(g)} \) from the following data

<table>
<thead>
<tr>
<th>Quantity</th>
<th>( \text{SOCl}_2(l) )</th>
<th>( \text{H}_2\text{O(l)} )</th>
<th>( \text{SO}_2(g) )</th>
<th>( \text{HCl(g)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S^0_{298} \text{(J mol}^{-1}\text{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 \text{ at 298 K kJ mol}^{-1} )</td>
<td>-245.6</td>
<td>-241.8</td>
<td>-296.8</td>
<td>-92.3</td>
</tr>
</tbody>
</table>

(Ans : \( \Delta S^0_{298} = 336.1 \text{ J mol}^{-1} \text{ K}^{-1} \);

\( \Delta H^0_{298K} = 6 \text{ kJ mol}^{-1}, \Delta G^0_{298K} = -94.15 \text{ kJ mol}^{-1} \)

Ans: \( \Delta G^0, \Delta H^0, \Delta S^0 \) for the reaction

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

\( = 6 \text{ kJ/mol} \)

\( \Delta S^0_{298} = 336.1 \text{ J K}^{-1}\text{ mol}^{-1}; \Delta G^0_{298} = 6000 - (298) (336.1) = -94.15 \text{ kJ mol}^{-1} \)

6. 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. (Ans : 23 kJ/mol).

Ans: \( dG = VdP - SdT \)

\( \Delta G = -S(T_2 - T_1) \)

\( = -230 (600 - 500) = -2300 \text{ J/mol.} \)

7. From the given data predict whether the reaction

\( \text{C}_2\text{H}_4(g) + \text{H}_2\text{O(l)} \rightarrow \text{C}_2\text{H}_5\text{OH(l)} \)

is spontaneous.
\( \Delta H^0_f \) (kJ/mol) \hspace{1cm} \( S^0 \) (J/K/mol)

\[
\begin{array}{ccc}
\text{C}_2\text{H}_5\text{OH} (l) & -277.69 & 160.7 \\
\text{H}_2\text{O}(l) & -285.83 & 69.91 \\
\text{C}_3\text{H}_4(g) & 52.26 & 291.56 \\
\end{array}
\]

\( \text{Ans: } 15.7 \text{ kJ, nonspontaneous} \)

\[
\Delta S^0 = 160.7 - (69.91 + 291.56)
\]
\[
= -200.77 \text{ JK}^{-1}\text{mol}^{-1}
\]
\[
\Delta H^0 = -277.69 - (-285.83 + 52.26)
\]
\[
= -44.12 \text{ kJ mol}^{-1}
\]
\[
\Delta G^0 = -44120 - (298) (-200.77)
\]
\[
= 15.709 \text{ J mol}^{-1}
\]
\( = + \text{ ve } \cdot \text{ non-spontaneous in the direction specific.} \)

8. 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 \(- 124 \text{ kJ, respectively. Calculate the values of } \Delta H \text{ and } \Delta S \text{ assuming that they do not vary with temperature.} \)

\( \text{Ans: } T_1 = 500 \text{ K; } T_2 = 510 \text{ K.} \)
\( \Delta G^0_{T2} = -124 \text{ kJ} \)
\( \Delta G^0_{T1} = -122 \text{ kJ} \)
\( \Delta G^0_{T2} / T_2 - \Delta G^0_{T1} / T_1 = \Delta H^0 \times [1/510 - 1/500] \)
\( -124/510 + 122/500 = \Delta H^0 (-10)/500 \times 510 \)
\( -0.2431 + 0.244 = \Delta H^0 (-3.92 \times 10^{-5}) \)
\( \Delta H^0 = 9 \times 10^{-4} / -3.92 \times 10^{-5} \)
\( = -2.296 \text{ kJ.} \)
\( \therefore \Delta G^0_{500 \text{ K}} = -22.96 - (500) \text{ kJ} \)
\( \therefore \Delta S^0 \text{ at } 500 \text{ K } \approx 0.198 \text{ kJ} \)

9. 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 \( \Delta H^0 \)

\( \text{Ans : } \Delta H^0 = -58.53 \text{ kJ/mol} \)

\[
\text{Ans: } d \ln k/d(1/l) = -\Delta H^0 / R
\]
\[\therefore \Delta H^0 = 58.53 \text{ kJ mol}^{-1}\]

10. The equilibrium constant of the reaction C (graphite ) + 2 H\(_2\)(g) = CH\(_4\)(g), at 35\(^0\)C is \(3.036 \times 10^8\) and \( \Delta H^0 \) for the reaction in the temperature range 25 – 35\(^0\)C is 179 k cal. Calculate \( \Delta G^0 \) at 25\(^0\)C.

\( \text{Ans : } \Delta G^0 = -5820 \text{ cal }\)

\[
\text{Ans: } K_p \text{ at } 308 \text{ K } = \text{ given}
\]
\[
\Delta G^0_{308} = -RT \ln (3.036 \times 10^8)
\]
\[
= -2 \times 308 \times 19.5312 \text{ cal mol}^{-1}
\]
\[
= -12.031 \text{ kcal mol}^{-1}\]
\[ \frac{\Delta G_{308}}{308} - \frac{\Delta G_{298}}{298} = \Delta H^0 (1/308 - 1/298) \]
\[ -12.031/308 - \frac{\Delta G_{298}}{298} = 179 (-10)/(298)(308) \]
\[ \therefore \Delta G_{298} \approx -5.82 \text{ k.cal.} \]
11. Construct the phase diagram of a two component system forming simple eutectic. Apply the phase rule in each region. Draw the cooling curve 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.

![Phase diagram of a two-component system forming a simple eutectic.](image)

12. 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$_2$O at its triple point

(Ans: 273.01 K & 4.52 torr; 45.2, 51.1 & 5.9 kJ mol$^{-1}$)

Ans: At the triple point temperature,
\[24.00 - 6140.1 / T = 21.41 - 5433 / T\]
\[\therefore 6140.1 / T - 5433 / T = 2.59\]
\[\therefore T = 273.01 \text{ K.}\]
Substituting in any of the equations, we obtain the triple point pressure as
\[\ln P = 24.00 - 6140.1 / 273.01\]
\[\therefore P \simeq 4.52 \text{ Torr.}\]

From the first eqn, \(d \ln p / dT = 6140.1 / T^2 = \Delta H^0 \text{ (sublimation)}/RT^2\)
\[\therefore \Delta H^0_{\text{sub}} = 6140.1 \times 8.314 = 51.05 \text{ kJ mol}^{-1}\]
From the second eqn, \(d \ln p / dT = 5433 / T^2 = \Delta H^0 \text{ (vap)}/RT^2\)
\[\therefore \Delta H^0_{\text{vap}} = 45.17 \text{ kJ mol}^{-1}\]
\[\therefore \Delta H^0 \text{ (fusion)} = 51.05 - 45.17 = 5.88 \text{ kJ mol}^{-1}\]

13. Calculate the change in entropy of a mole of aluminium (at.wt .27) which is heated from 600 to 700$^0$ C. The m.pt .of Al is 660$^0$ C, the heat of fusion is 393 J$^{-1}$ 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$^{-1}$)

\[\Delta S = C_p \ln T_m / T_1 + \Delta H_f / T_m + C_p \ln T_2 / T_m\]
\[\Delta H_f = 393 \text{ J gm}^{-1} = 10.611 \text{ kJ mol}^{-1}\]
\[\therefore \Delta S \approx 31.8 \ln 933/873 + 10611/933 + 34.4 \ln 973/933\]
\[\therefore \Delta S \approx 14.93 \text{ JK}^{-1} \text{ mol}^{-1}\]

14. Based on the Trouton’s rule, calculate the molar heat of vapourisation of benzene at its boiling point of 353 K (Ans: 31 kJ)

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

15. 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$^{-1}$)

\[C_v = 3R/2 + 3R/2 + 3R \approx 49.88 \text{ JK}^{-1} \text{ mol}^{-1}\]

16. For the reaction CO$_2$ (g) + H$_2$ (g) $\square$ CO$_2$(g) + H$_2$O (g) \(K_p\) is 0.63 at 700$^0$ C and 1.66 at 100$^0$ C. a) What is the average value of \(\Delta H\) in this temperature range ? b) What is the value of \(K_p\) at 800$^0$C ?

(Ans : \(\Delta H = 1.17 \times 10^3\text{cal, } K_p= 0.67\))
Ans: \( \ln K_p(T_2)/K_p(T_1) = \Delta H^0(T_2 - T_1)/R T_1 T_2 \)
\( K_p(973 \text{K}) = 0.63; \) \( K_p(373 \text{K}) = 1.66 \)
\( \Delta H^0 = -1.17 \times 10^3 \text{cal} \)
\( \ln [K_p(1073 \text{K})/0.63] = \Delta H^0/R (1073 - 973)/(1073 \times 973) \)
\( \therefore K_p \text{ at } 1073 \text{K} \approx 0.67 \)

17. 100 g N\(_2\) at 300 K were held by a piston at 30 atm. Pressure was released suddenly to become 10 atm, adiabatically. Calculate \( \Delta S \). \( C_V = 20.8 \text{JK}^{-1}\text{mol}^{-1} \).

\[ \Delta S = n(C_V \ln T_2/T_1 + R \ln V_2/V_1) \]

Sudden adiabatic expansion, \( T_2 \) is unknown.
\[ V_2/V_1 = T_2 P_1/T_1 P_2 = 217.8 \]
\[ \Delta S = -0.692 \text{JK}^{-1} \]

18. Calculate entropy change when 0.5 L ideal gas, \( C_V = 12.6 \text{JK}^{-1}\text{mol}^{-1} \), at 300 K and 1 atm was allowed to expand to double its volume while heated simultaneously to 373 K.

\[ \Delta S = n(C_V \ln T_2/T_1 + R \ln V_2/V_1) \]
\[ \Delta S = 0.17 \text{JK}^{-1} \]

19. 10 g ice at 0 oC are added to 20 g water at 90 oC, in a thermally insulated flask of negligible heat capacity. Heat of fusion of ice is 6 kJ mol\(^{-1}\). Calculate the final temperature and the entropy change of the system. \( C_p = 75.42 \text{JK}^{-1}\text{mol}^{-1} \).

10 g H\(_2\)O (s), 273 K \( \rightarrow \) H\(_2\)O(l) 273 K \( \rightarrow \) H\(_2\)O(l), T K. Two entropy changes, \( \Delta S_1 \), \( \Delta S_2 \)
90 g H\(_2\)O(l) 363 K \( \rightarrow \) H\(_2\)O(l), T K, \( \Delta S_3 \)

Heat balance equation, \( nL_f + C_p(T-273) = nC_p(363-T); T = 306.5 \)

\[ \Delta S_1 = nL_f/T = 12.2 \text{JK}^{-1} \]
\[ \Delta S_2 = n(C_p \ln T_2/T_1) = 4.85 \text{JK}^{-1} \]
\[ \Delta S_3 = n(C_p \ln T_2/T_1) = -14.31 \text{JK}^{-1} \]
\[ \Delta S = \text{sum} = 2.75 \text{JK}^{-1}, \text{corresponds only to the system} \]

20. In an open beaker held at 27 oC and 1 at pressure containing dilute sulphuric acid, 100 g zinc were added. Calculate the work done by the liberated gas. Calculate the work done if the reaction was carried out in a closed container.

\[ \text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2 \]
\[ \text{W}_{r, \text{irr}} = \Delta nRT = 100/65 \times 8.314 \times 300 = 3.84 \text{kJ} \]
Closed container, no volume change, no work.
21. A balloon containing air at 1 atm pressure is 0.5 m in diameter. It was isothermally filled with air so that the pressure is 5 atm. Assuming the pressure is proportional to the diameter of the balloon, calculate the (a) final diameter and (b) work done in the process.

\[ P \propto d \]
\[ d_{\text{final}} = 2.5 \text{ m} \]
\[ P = kd = k = 2 \text{ atm m}^{-1} \]
\[ dW = P \, dV = kd \cdot 3 \left(4\pi\right) \left(\frac{d}{2}\right)^2 \, dd = k\pi/2 \, d^3 \, dd \]
\[ W = k\pi/2 \int \left[0.5 \, 2.5 \, d^3 \, dd - k\pi/8 \left[2.5^4 - 0.5^4\right]\right] = [2\text{ atm m}^{-1} \times \pi/8] \times 39 = 30.63 \text{ atm m}^3 \]
\[ = 3.1 \times 10^6 \text{ J} \]

22. The entropy change of argon is given to a good approximation by the expression, \( S \text{ JK}^{-1} \text{ mol}^{-1} = 36.36 + 20.79 \ln T \)

Calculate change in Gibb’s free energy of one mole of argon gas if it is heated at constant pressure from 25 °C to 50 °C.

\[ dG = VdP - SdT \text{ at constant } P, \quad dG = -SdT \]
\[ \int dG = -[36.36dT + 20.79\ln TdT] = -36.36 \left(T_2 - T_1\right) - 20.79 \left[T\ln T - T_1\right]^{T_2} \]
\[ = -999 - 20.79 \left(1543.18 - 1399.73\right) = -3891.33 \text{ J} \]

23. 1 mole of ideal gas initially at 10 atm and 300 K was expanded adiabatically against a constant pressure of 4 atm so as to reach equilibrium. \( C_p = 28.48 + 1.76 \times 10^{-2} \text{ T J mol}^{-1} \).

Calculate \( \Delta U, \Delta H \) and \( \Delta S \).

\[ C_V = 20.17 + 1.76 \times 10^{-2} \text{ T} \]
\[ dU = C_V \, dT = PdV \]
\[ \Delta U = 20.17 \left(T_2 - T_1\right) + 1.76/2 \times 10^{-2} \left(T_2^2 - T_1^2\right) = P_2 \left(V_2 - V_1\right) = P_2 \left(R\left(T_1/P_1 - T_2/P_2\right)\right) = R \left(P_2T_1/P_1 - T_2\right) \]

We can now solve for \( T_2 \).
\[ T_2 = 255.3 \text{ K} \]

\[ dS = C_p \, dT/T - R \frac{dP}{P} = (28.58 + 1.76 \times 10^{-2} \text{ T}) \, dT/T - R \frac{dP}{P} \]
\[ \Delta S = 28.58 \ln T_2/T_1 + 1.76 \times 10^{-2} \left(T_2 - T_1\right) + R \ln P_1/P_2 = 2.22 \text{ JK}^{-1} \]

\[ \Delta U = \int C_V \, dT = -1124.3 \text{ J} \]
\[ \Delta H = \int C_p \, dT = -1496 \text{ J} \]

24. One mole of ideal gas was subjected to the following change. \( A \rightarrow B \rightarrow C \) (Details of \( P, T \) and \( V \) can be given here). Depict the above process in a P-V diagram, determine the net work done in the cyclic process. \( C_V = 1.5R \).

References: Suggested books for CY101
All the details of the points A, B, C may not be given. You will have to calculate all using ideal gas law.

25. Manipulation of Maxwell’s relations, cyclic rule \((\partial T/\partial P)s(\partial P/\partial S)_T(\partial S/\partial T)_P = -1\)

26. Entropy of mixing

27. Calculation of partition functions:
Assume that 1000 particles are distributed in 5 energy levels, which are equally spaced with the spacing as XX. The ground state energy is zero. What is the total energy at \(T = 300\) K.

\[
N = 1000 \\
Ni/N = e^{-Ei/kT} / \sum e^{-Ei/kT}
\]

Calculate \(N_i\)’s

\[
E = \sum N_i E_i
\]

Use of this in calculating U