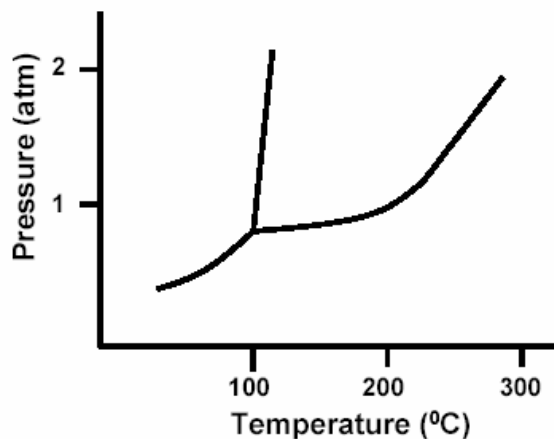


- When a gas is expanded adiabatically to a larger volume and a lower pressure, the volume is smaller than it would be after an isothermal expansion under identical conditions. **(Ans: True)**
- The statement $dS < \frac{\partial q}{T}$ corresponds to spontaneous and irreversible process. **(Ans: False)**
- The entropy for mixing equal volumes of the same ideal gas at constant temperature and pressure will be ----- **(Ans: zero)**
- Translation partition function for a molecule is an ----- variable **(Ans: extensive)**
- The internal pressure $\left(\frac{\partial U}{\partial V}\right)_T$ of an ideal gas is zero. If attractions are dominant in a real gas, the internal energy **(Ans: a)**
(a) Increases with the increase in volume.
(b) Decreases with the increase in volume.
- An adiabatic process is _____ **(Ans: b)**
(a) Isoenthalpic (b) Isoentropic (c) isobaric (d) isochoric
- Consider two reversible Carnot engines A and B. Engine A uses a real gas and engine B uses an ideal gas. If the two engines operate between the same temperature limits T_1 and T_2 ($T_2 > T_1$), then which one is true? **(Ans: c)**
(a) The efficiency of A will be greater than B.
(b) The efficiency of A will be less than B.
(c) The efficiency of A will be equal to B.
(d) Cannot be predicted.
- What are the maximum number of phases that can be in equilibrium with each other in a two component system? **(Ans: c)**
(a) 2 (b) 3
(c) 4 (d) 5
- For which of these processes is the value of ΔS negative? **(Ans: b)**
I. Sugar is dissolved in water.
II. Steam condenses on a surface.
III. CaCO_3 is decomposed into CaO and CO_2 .
(a) I only (b) II only
(c) I and III only (d) II and III only

10. Which statement is correct about the substance represented by this phase diagram?

(Ans: d)



- (a) The solid sublimates at 1 atm pressure.
 (b) Its normal boiling point is above 300°C.
 (c) It exists as a liquid at 80°C and 1 atm.
 (d) The density of the solid is greater than that of the liquid.
11. 3.0 moles of an ideal gas expands isothermally (in thermal contact with the surroundings; temperature = 15°C) against a fixed external pressure of 1.0 bar. The initial and final volumes of the gas are 10.0L and 30.0L, respectively. Calculate change in the entropy of the system, surroundings and the universe.

Ans. Since ΔS_{sys} is independent of path, it is the same as for isothermal reversible expansion of an ideal gas

$$\Delta S_{sys} = nR \ln \frac{V_f}{V_i} = 3R \ln 3$$

$$\Delta S_{sys} = 27.4 JK^{-1}$$

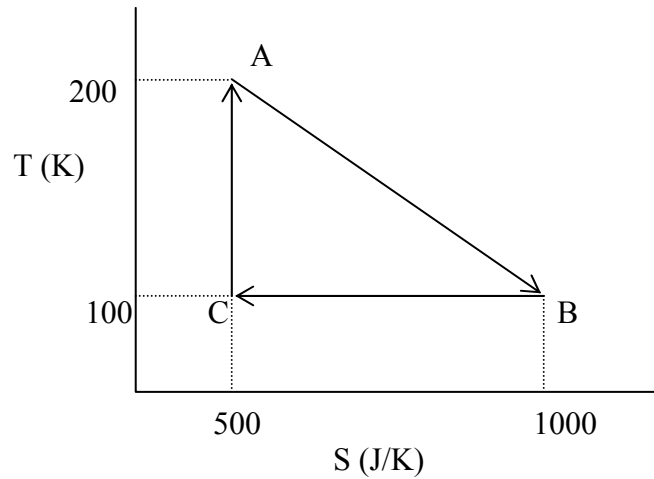
$$q = p_{ext} \Delta V$$

$$\Delta S_{surr} = -\frac{q}{T}$$

$$= -6.94 JK^{-1}$$

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} = 20.5 JK^{-1}$$

12. What is the efficiency for a reversible engine operated around the cycle illustrated? (For step A to B, consider the mean temperature of 150K)



Ans.

$$\begin{aligned}
 Q_{BC} &= \int_B^C T dS = \frac{300}{2} \times 500 = 75,000 J \\
 Q_{CA} &= -100 \times 500 = -50,000 J \\
 Q_{AB} &= 0 \\
 \eta &= \frac{\text{work}}{Q_{BC}} = \frac{Q_{BC} + Q_{CA}}{Q_{BC}} = \frac{1}{3} \text{ or } 33.3\%
 \end{aligned}$$

13. Two phases, α and β , of a pure substance exist in equilibrium at constant temperature and pressure. Starting from the fundamental equation for Gibbs energy, prove that $\mu_\alpha = \mu_\beta$ where μ is the chemical potential.

$$dG = -SdT + VdP + \sum_{i=1}^{N_s} \mu_i dn_i$$

For two phases, α and β at constant T and P, the change in Gibbs free energy upon transferring an infinitesimal amount of dn_i from α to β , is given by:

$$(dG)_{T,P} = -\mu_i(\alpha)dn_i + \mu_i(\beta)dn_i = dn_i[\mu_i(\beta) - \mu_i(\alpha)]$$

At equilibrium,

$$(dG)_{T,P} = dn_i[\mu_i(\beta) - \mu_i(\alpha)] = 0$$

$$\Rightarrow \mu_i(\alpha) = \mu_i(\beta)$$

(In this particular problem $i=1$)

14. Calculate the pressure of CO_2 gas at 700K in the heterogeneous equilibrium reaction given below, if ΔG^0 for this reaction is $130.2 \text{ kJ mol}^{-1}$.



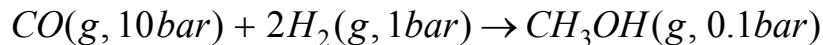
Ans :

$$K_P = p_{\text{CO}_2}$$

$$\Delta G^0 = -RT \ln(K_P)$$

$$\Rightarrow K_P = e^{-\frac{\Delta G^0}{RT}} = e^{-\frac{130200 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 700 \text{ K}}} = 1.94 \times 10^{-10}$$

15. A mixture of $\text{CO}(\text{g})$, $\text{H}_2(\text{g})$ and $\text{CH}_3\text{OH}(\text{g})$ at 500K with $p(\text{CO})=10 \text{ bar}$, $p(\text{H}_2)=1 \text{ bar}$ and $p(\text{CH}_3\text{OH})=0.1 \text{ bar}$ is passed over a catalyst. Is this reaction thermodynamically feasible? Given: $\Delta G^0=21.21 \text{ kJ mol}^{-1}$ and



Ans :

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2} \right)$$

$$\Delta G = 21.21 \text{ kJ mol}^{-1} + 0.008314 \text{ kJ mol}^{-1} \times 500 \text{ K} \times \ln \left(\frac{0.1}{10 \times 1^2} \right)$$

$$\Delta G = 2.07 \text{ kJ mol}^{-1}$$

ΔG is positive, hence the reaction is not possible and therefore no methanol will be formed!

16. Using the Maxwell's relations obtained from the basic thermodynamic relations $dH=TdS+VdP$ and $dG=VdP-SdT$, and cyclic rule,

$$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1$$

show that for an ideal gas, $\left(\frac{\partial V}{\partial S}\right)_P = \frac{nRT}{PC_P}$

Using the cyclic rule,

$$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1, \quad \left(\frac{\partial T}{\partial P}\right)_S = -\frac{1}{\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P}$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} \text{-----(1)}$$

We have $dS = C_P \frac{dT}{T} \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$

Substituting for $\left(\frac{\partial S}{\partial T}\right)_P$ in (1) we get,

$$\left(\frac{\partial T}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\frac{C_P}{T}} = -\frac{T\left(\frac{\partial S}{\partial P}\right)_T}{C_P} \text{-----(2)}$$

Now, from $dH = TdS + VdP$, one can derive the Maxwell's relation,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Substituting for $\left(\frac{\partial T}{\partial P}\right)_S$ in (2) we get,

$$\left(\frac{\partial V}{\partial S}\right)_P = -\frac{T\left(\frac{\partial S}{\partial P}\right)_T}{C_P} \text{-----(3)}$$

From $dH = VdP - SdT$, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Substituting for $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P} \text{-----(4)}$$

We have $PV = nRT \Rightarrow V = \frac{nRT}{P}$

Substituting for V in (4), we get,

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P} = \frac{nRT}{C_P T}$$

17. The standard reaction Enthalpy of $\text{Zn(s)} + \text{H}_2\text{O(g)} \rightarrow \text{ZnO(s)} + \text{H}_2\text{(g)}$ is approximately constant at $+224\text{kJmol}^{-1}$ from 920K up to 1280K . The standard reaction Gibbs energy is $+33\text{kJ mol}^{-1}$ at 1280K . Estimate the temperature at which the equilibrium constant becomes 1.

Ans :

$$\ln K_1(1280\text{K}) = -\frac{\Delta_r G^0}{RT} = \frac{33000\text{J mol}^{-1}}{(8.314\text{JK}^{-1}\text{mol}^{-1}) \times 1280\text{K}}$$

$$\Rightarrow K_1 = 0.045$$

$$\text{We have, } \ln K_2 = \ln K_1 - \frac{\Delta_r H^0}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (\text{Van't Hoff's equation})$$

We want a temperature T_2 that corresponds to $\ln K_2 = \ln(1) = 0$.

This is the cross over temperature.

Now, keeping $\ln K_2 = 0$, and solving for T_2 ,

$$\frac{1}{T_2} = \frac{R \ln K}{\Delta_r H^0} + \frac{1}{T_1} = \frac{8.314\text{JK}^{-1}\text{mol}^{-1} \times \ln(0.045)}{224000\text{Jmol}^{-1}} + \frac{1}{1280\text{K}}$$

$$\Rightarrow T_2 = 1501\text{K}$$

18. N particles are distributed among three states having energies $E_1 = 0$, $E_2 = kT$ and $E_3 = 2kT$. If the total energy of the system is $1000kT$, what is the value of N?

Ans.

Ist Method:

$$P_i = \frac{N_i}{N} = \frac{e^{-E_i/kT}}{\sum_{i=1}^3 e^{-E_i/kT}}$$

$$N_1 = \frac{N}{(1 + 1/e + 1/e^2)}$$

$$N_2 = \frac{N}{(1 + 1/e + 1/e^2)} 1/e$$

$$N_3 = \frac{N}{(1 + 1/e + 1/e^2)} 1/e^2$$

$$E = E_1 N_1 + E_2 N_2 + E_3 N_3$$

$$E = \frac{NkT}{1 + 1/e + 1/e^2} (1/e + 2/e^2)$$

$$E = 1000kT$$

$$N = \frac{1000(1 + e^{-1} + e^{-2})}{e^{-1} + 2e^{-2}} \approx 2400$$

IInd Method:

$$P_i = \frac{N_i}{N} = \frac{e^{-E_i/kT}}{\sum_{i=1}^3 e^{-E_i/kT}}$$

$$\bar{E} = \sum_i E_i P_i$$

$$= \frac{kT(1/e + 2/e^2)}{1 + 1/e + 1/e^2}$$

$$E = N\bar{E}$$

$$E = 1000kT$$

$$N = \frac{1000(1 + e^{-1} + e^{-2})}{e^{-1} + 2e^{-2}} \approx 2400$$