

1. State the principle of corresponding states for gases and use van der Waals equation for a real gas to illustrate it.

Ans. The principle of corresponding states for gases says that gases confined to the same reduced volume, V_r , at the same reduced temperature, T_r , would exert the same reduced pressure, p_r , where $V_r = \frac{V_m}{V_c}$; $p_r = \frac{p}{p_c}$; $T_r = \frac{T}{T_c}$

van der Waals equation : $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \implies p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2} \dots\dots (A)$

At critical conditions, $p-V$ isotherms go through a point of inflection. $\therefore \frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$ and $\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$

Simplifying, we get, $V_c = 3b$, $T_c = \frac{8a}{27Rb}$ and $p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{a}{27b^2}$

\therefore Using (A), $\frac{ap_r}{27b^2} = \frac{\frac{8aT_r}{27b}}{3bV_r - b} - \frac{a}{9b^2V_r^2} \implies p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$

If isotherms are plotted in terms of the reduced variables, then the same curves are obtained whatever the gas. This is precisely the content of the principle of corresponding states.

2. (a) Discuss Landauer's principle of information loss.

Ans. The Landauer principle quantifies the thermodynamic cost of the recording/erasure of one bit of information :
"information is physical" and it has an energy equivalent.

Erasure of one bit of information requires a minimum energy cost equal to $k_B T \ln 2 \approx 0.018 \text{ eV}$, where T is the temperature of a thermal reservoir used in the process.

(1) any logically irreversible process must result in an entropy increase in the non-information-bearing degrees of freedom of the information-processing system or its environment

(2) any logically reversible process can be implemented thermodynamically reversibly.

- an amount of energy equal to $k_B T \ln 2$ ($k_B T$ = thermal noise per unit bandwidth) is needed to transmit a bit of information, and more if quantized channels are used with photon energies $h\nu > kT$

- (b) Organization and complexity increases in biological evolution. Does this violate the second law of thermodynamics? Explain. 1

Ans. Organization and complexity increases and entropy decreases in biological evolution. However, this does not violate the second law of thermodynamics because the entropy principle refers to isolated systems only, and the earth is not an isolated system or closed system. While species may be becoming more ordered, the universe as a whole becomes more disorganized for the sun releases energy and becomes disordered.

3. Statements, S_1 and S_2 are equivalent if violation of one implies the violation of the other **and vice versa**, i.e., $\neg S_1 \subset \neg S_2$, and $\neg S_2 \subset \neg S_1$. Use this method to prove the equivalence of the Kelvin-Planck and Clausius statements of the second law.1

Ans. Consider two heat reservoirs, at temperatures T_h and $T_l < T_h$.

Consider a refrigerator violating C, i.e., holding $\neg C$ as true.

It takes q_L heat from the cold source and dumps all of it to the hot sink. An engine takes q_H heat from the hot source and dumps q_L to the hot sink. It converts part of the heat, into work; $q_H(>0) + q_L(<0) = w$ satisfying K.

Form a composite system consisting of the two devices put together. It takes

$q_H(>0) + q_L(<0)$ amount of heat from the hot source and converts it completely into

work, thus violating K. $\therefore -C \subset -K$,

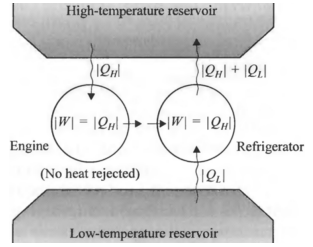
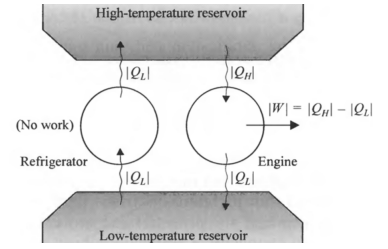
Consider an engine violating K, i.e, holding $-K$ as true.

It takes q_H amount of heat from the hot source and converts it completely into work.

A refrigerator takes q_L heat from the cold source and we add work $w = q_H(>0)$ to it, dumping $q_H + q_L$ into the hot sink, satisfying C.

Form a composite system consisting of the two devices put together. It takes q_L heat from the cold source and dumps it into the hot sink, thus violating C. $\therefore -K \subset -C$

Hence, $K \equiv C$.



4. (a) Starting from definition of Helmholtz free energy, A , derive : $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

and (c) show that the difference of heat capacities, $C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$, where α = thermal expansion coefficient and κ_T = isothermal compressibility.

Ans. $A = U - TS$

$$dA = dU - TdS - SdT = dU - dq - SdT \text{ (Using 2nd law)} = -pdV - SdT \text{ (work only mechanical [p-V])}$$

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

A is a state function and dA is an exact differential

$$\therefore \text{when both } T \text{ and } V \text{ vary, } \frac{\partial^2 A}{\partial T \partial V} = \frac{\partial^2 A}{\partial V \partial T} \implies \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

- (b) find how the entropy depends on volume for a van der Waals gas,

$$\text{Ans. } p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \implies \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\therefore S = \int \frac{nR}{V-nb} dV = nR \ln(V-nb) + \text{const.}$$

(c) show that the difference of heat capacities $C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$, where α = thermal expansion coefficient and β = isothermal compressibility.

$$\text{Ans. } C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial[U+pV]}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= (\alpha\pi_T V + C_V) + p\left(\frac{\partial V}{\partial T}\right)_p - C_V = \alpha\pi_T V + p\left(\frac{\partial V}{\partial T}\right)_p = \alpha(p + \pi_T)V$$

$$\text{starting with } dU = TdS - pdV \implies \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \quad \text{or, } \pi_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

$$\text{Using the relation } \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \implies \pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\therefore C_p - C_V = \alpha TV \left(\frac{\partial p}{\partial T}\right)_V$$

$$\text{Also, } \therefore dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp; \therefore \text{at const. } V, dV = 0 \implies \left(\frac{\partial V}{\partial T}\right)_p dT = -\left(\frac{\partial V}{\partial p}\right)_T dp, \text{ or, } \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$\therefore \left(\frac{\partial p}{\partial T} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = \frac{\alpha}{\kappa_T} \text{ and } \therefore C_p - C_V = \alpha TV \left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha^2 TV}{\kappa_T}$$

5. Suppose that for a certain phase transition of a solid $\Delta_{\text{trs}} V = +1.0 \text{ cm}^3 \text{ mol}^{-1}$ is independent of pressure. By how much does that Gibbs energy of transition change when the pressure is increased from 1.0 bar to 3.0 Mbar ($\text{M} \equiv 10^6$)?

Ans. Label the phases as 1 and 2.

$$G_{\text{m},1}(p_f) = G_{\text{m},1}(p_i) + \int_{p_i}^{p_f} V_{\text{m},1} dp$$

$$G_{\text{m},2}(p_f) = G_{\text{m},2}(p_i) + \int_{p_i}^{p_f} V_{\text{m},2} dp$$

$$G_{\text{m},2} - G_{\text{m},1} = \Delta_{\text{trs}} G \text{ and } V_{\text{m},2} - V_{\text{m},1} = \Delta_{\text{trs}} V:$$

$$\Delta_{\text{trs}} G_{\text{m}}(p_f) = \Delta_{\text{trs}} G_{\text{m}}(p_i) + \int_{p_i}^{p_f} \Delta_{\text{trs}} V_{\text{m}} dp$$

$\Delta_{\text{trs}} V$ is independent of pressure \implies

$$\begin{aligned} \Delta_{\text{trs}} G_{\text{m}}(p_f) &= \Delta_{\text{trs}} G_{\text{m}}(p_i) + \Delta_{\text{trs}} V_{\text{m}} \int_{p_i}^{p_f} dp \\ &= \Delta_{\text{trs}} G_{\text{m}}(p_i) + \Delta_{\text{trs}} V_{\text{m}} (p_f - p_i) \end{aligned}$$

Inserting the data gives

$$\begin{aligned} \Delta_{\text{trs}} G(3 \text{ Mbar}) &= \Delta_{\text{trs}} G(1 \text{ bar}) + (1.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times \\ &\quad (3.0 \times 10^{11} \text{ Pa} - 1.0 \times 10^5 \text{ Pa}) \\ &= \Delta_{\text{trs}} G(1 \text{ bar}) + 3.0 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

where we have used $1 \text{ Pa m}^3 = 1 \text{ J}$.

6. Beginning with $U \equiv U(S, V, N)$, where the letters for variables carry the usual meaning, and an isolated chamber with two compartments separated by a 'wall', derive the directions for changes in temperature, pressure and number of moles and the conditions for thermal, mechanical and chemical equilibria.

Ans. isolated system : internal energy, U , total volume, V and total mass of the one component, N (no. of moles) are constant

$$dU = TdS - pdV + \mu dN, \text{ or, } dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN; \text{ For equilibrium, } dS = 0$$

$$U = U^{(1)} + U^{(2)} = \text{const, or, } dU = dU^{(1)} + dU^{(2)} = 0; V = V^{(1)} + V^{(2)} = \text{const, or, } dV = dV^{(1)} + dV^{(2)} = 0$$

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$$N = N^{(1)} + N^{(2)} = \text{const, or, } dN = dN^{(1)} + dN^{(2)} = 0 \text{ and}$$

$$dS = dS^{(1)} + dS^{(2)} = \frac{1}{T^{(1)}}dU^{(1)} + \frac{1}{T^{(2)}}dU^{(2)} + \frac{p^{(1)}}{T^{(1)}}dV^{(1)} + \frac{p^{(2)}}{T^{(2)}}dV^{(2)} - \frac{\mu^{(1)}}{T^{(1)}}dN^{(1)} - \frac{\mu^{(2)}}{T^{(2)}}dN^{(2)}$$

To explore thermal equilibrium, consider only heat flow :

$$\text{impermeable, rigid, diathermal wall} \implies dV^{(1)} = dV^{(2)} = 0 \text{ and } dN^{(1)} = dN^{(2)} = 0$$

$$\therefore dU^{(1)} + dU^{(2)} = 0 \implies dU^{(1)} = -dU^{(2)} = dU \text{ (say) } \therefore dS = \frac{1}{T^{(1)}}dU - \frac{1}{T^{(2)}}dU = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU \geq 0$$

if $dU > 0$ (flow of energy from phase 2 to phase 1),

then $T^{(1)} < T^{(2)}$, i.e. energy must flow from higher to lower temperature for thermal equilibrium to be reached

At $T^{(1)} = T^{(2)}$ (thermal equilibrium), $dS = 0$

to explore mechanical equilibrium, consider flexible, impermeable, diathermal wall with $T^{(1)} = T^{(2)} = T$ and $dN^{(1)} = dN^{(2)} = 0$

$$\because dV^{(1)} + dV^{(2)} = 0 \implies dV^{(1)} = -dV^{(2)} = dV \text{ (say)}, \therefore dS = \frac{p^{(1)}}{T}dV - \frac{p^{(2)}}{T}dV = \frac{1}{T} (p^{(1)} - p^{(2)}) dV \geq 0$$

if $dV > 0$ (wall moves away from phase 1 to phase 2),

then $p^{(1)} > p^{(2)}$, i.e. mechanical equilibrium requires movement of the wall from higher pressure to lower pressure region

When $p^{(1)} = p^{(2)}$ (mechanical equilibrium), $dS = 0$

to explore chemical equilibrium. consider the systems 1 and 2 at thermal and mechanical equilibrium with flexible, permeable,

diathermal wall, s.t. $T^{(1)} = T^{(2)} = T$ and $p^{(1)} = p^{(2)} = p$

$$\because dN^{(1)} + dN^{(2)} = 0 \implies dN^{(1)} = -dN^{(2)} = dN \text{ (say)}, \therefore dS = -\frac{\mu^{(1)}}{T}dN^{(1)} + \frac{\mu^{(2)}}{T}dN = \frac{1}{T} (\mu^{(2)} - \mu^{(1)}) dN \geq 0$$

if $dN > 0$ (mass moves from phase 2 to phase 1)

then $\mu^{(2)} > \mu^{(1)}$, i.e., mass moves spontaneously from higher to lower chemical potentials

When $\mu^{(1)} = \mu^{(2)}$ (chemical equilibrium), $dS = 0$

7. Is the pH of 1 M HCl (aq) zero or non-zero? Explain.

Ans. The pH is defined as $\text{pH} = -\log_{10} a_{\text{H}^+}$, where a_{H^+} = activity of hydrogen ions in the solution.

For solutions that are not dilute, $a_{\text{H}^+} = \gamma \cdot c_{\text{H}^+}$, where c_{H^+} = molarity of hydrogen ions.

For 1 M HCl (aq), $a_{\text{H}^+} = \gamma \cdot 1$ and $\gamma \neq 1$ (for HCl, $\gamma \lesssim 1$) $\therefore \text{pH} \neq 0$

8. At absolute zero of temperature, a pair of carbon monoxide molecules may assume one of two possible configurations - identical atoms or hetero atoms next to each other. Estimate the residual entropy for carbon monoxide.

Ans. For a pair of molecules, with two arrangements possible, $S = k_B \ln 2$

\therefore residual entropy for CO = $\frac{1}{2} R \ln 2 \text{ mol}^{-1} = \frac{1}{2} \times 8.314 \times 0.693 = 2.881 \text{ J mol}^{-1} \text{ K}^{-1}$.