Thermodynamics: Classical to Statistical
Prof. Sandip Paul
Department of Chemistry
Indian Institute of Technology Guwahati
Lecture - 34
Advance Problems - 2

Problem 10:

The vapor pressure of liquid decane is 10 Torr at 55 ˚C temperature and 400 Torr at 150.6 ˚C. Calculate ΔH_v, ΔS_v at 100 ˚C and its normal boiling point.

Solution:

For liquid vapor equilibrium, we can write,

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Putting the values of P_2, P_1, T_1 and T_2 we can calculate ΔH.

$$\log \frac{400}{10} = \frac{\Delta H_v}{2.303R}\left(\frac{1}{328} - \frac{1}{423.6}\right)$$

$$\text{Or,} \quad \Delta H_v = 45kJ$$

At boiling point, $$\Delta S_v = \frac{\Delta H_v}{T}$$

$$\text{Or,} \quad \Delta S_v = \frac{45000}{373} JK^{-1} = 120.67\, JK^{-1}$$

Problem 11:

The variation of vapor pressure (in mm Hg) with absolute temperature for a given substance M is given by,

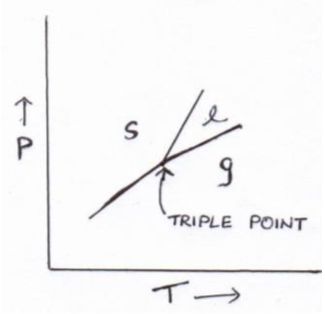
$$\log P = -\frac{2460}{T} + 6.69 \qquad \text{(for liquid M)}$$

$$\log P = -\frac{6947}{T} + 10.8 \qquad \text{(for solid M)}$$

Calculate the temperature and pressure corresponding to the triple point of substance M.

Solution:

At triple point the vapor pressure of liquid and solid states of substance M are equal.



Hence, we can write,

$$-\frac{2460}{T} + 6.69 = -\frac{6947}{T} + 10.8$$

$$\text{Or,} \quad T = 1091.7K$$

This is the temperature of the triple point. On substituting the value of T in any of the above two expressions, we get

P = 27323.11 mm of Hg = 35.95 atmosphere.

Problem 12:

Predict whether it is possible or not to reduce magnesium oxide using carbon at 298 K temperature according to the reaction

$$MgO\,(s) + C\,(s) \longrightarrow Mg\,(s) + CO\,(g)$$

$$\Delta_r H^\circ = 491.18 \text{ kJ mol}^{-1} \text{ and } \Delta_r S^\circ = 197.67 \text{ J K}^{-1}\text{mol}^{-1}$$

If not, at what temperature, the reaction becomes spontaneous?

Solution:

In order to check whether the reaction is feasible or not we need to calculate $\Delta_r G^\circ$.

$$\Delta_r G^\circ = \Delta_r H^\circ - T\,\Delta_r S^\circ \qquad (1)$$

At 298 K temperature,

$$\Delta_r G^\circ = 491.18\times1000 \text{ J mol}^{-1} - 298 \text{ K} \times 197.67 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\text{Or,} \quad \Delta_r G^\circ = 432.28 \text{ kJ mol}^{-1} > 0$$

Hence the reaction is not feasible at 298 K temperature.

At equillibrium, where $\Delta_r G^\circ = 0$, equation 1 can be written as,

$$T = \frac{\Delta_r \mathrm{H}^\circ}{\Delta_r S^\circ}$$

Or, $$T = \frac{491.18 \times 1000}{197.67} K$$

Or, $$T = 2484.8K$$

To have $\Delta_r G^\circ < 0$, we need to have temperature greater than 2484.8 K.

Thus above 2484.8 K temperature, the above reaction is feasible.

Problem 13:

For 1 mole of van Der Waals gas undergoing a reversible isothermal expansion from a volume V_1 to a final volume V_2, show that the heat transferred q is given by,

$$q = RT \ln \frac{V_2 - b}{V_1 - b}$$

Solution:

For 1 mole of van Der Waals gas, we can write,

$$\left(P + \frac{1^2 a}{V^2}\right)(V - 1 \times b) = 1 \times RT$$

Or, $$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Or, $$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

Or, $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Heat transferred,

$$\delta q = TdS$$

Or, $$q = \int TdS$$

$$\text{Or,}\quad q = \int T \left(\frac{\partial P}{\partial T} \right)_V dV$$

Since the process is isothermal,

$$q = T \int_{V_1}^{V_2} \frac{R}{V - b} dV$$

$$q = RT \ln \frac{V_2 - b}{V_1 - b}$$

Problem 14:

A gas obeys the equation of state,

$$\frac{PV}{RT} = 1 + PB(T)$$

where the B(T) is a function of temperature only. Show that

$$C_P - C_{P_{\circ}} = -RTP \frac{\partial^2 B(T)}{\partial T^2}$$

where $C_{P_{\circ}}$ is the value of C_P at some reference temperature.

Solution:

We know that,

$$\frac{\partial C_P}{\partial P} = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

$$\text{Or,}\quad C_P = -\int T \left(\frac{\partial^2 V}{\partial T^2} \right)_P dP$$

Given,

$$\frac{PV}{RT} = 1 + PB(T)$$

$$\text{Or,}\quad V = \frac{RT}{P} \left(1 + PB(T) \right)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}\left(1+PB(T)\right)+\frac{RT}{P}P\left(\frac{\partial B(T)}{\partial T}\right)_P$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = R\frac{\partial^2 B(T)}{\partial T^2}$$

$$C_P = -\int RT\frac{\partial^2 B(T)}{\partial T^2}dP = -RT\frac{\partial^2 B(T)}{\partial T^2}\int RT$$

Or, $$C_P = -RT\frac{\partial^2 B(T)}{\partial T^2}+\text{constant}$$

When P →0, $C_p \rightarrow C_{P_\circ}$. Hence the constant term of above expression is . Therefore we get,

$$C_P - C_{P_\circ} = -RTP\frac{\partial^2 B(T)}{\partial T^2}$$

Problem 15:

A substance expands in such a manner that its elasticity is equal to the sum of isothermal and adiabatic elasticity. Find the specific heat of the substance under this condition in terms of C_p and C_V.

Solution:

Let C_A be the specific heat of the substance under the given condition,

$$C_A = T\left(\frac{\partial S}{\partial T}\right)_A$$

Or, $$C_A = T\left[\frac{\left(\frac{\partial S}{\partial P}\right)_V dP+\left(\frac{\partial S}{\partial V}\right)_P dV}{\left(\frac{\partial T}{\partial P}\right)_V dP+\left(\frac{\partial T}{\partial V}\right)_P dV}\right]_A$$

Or, $$C_A = T\left[\frac{\left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_A+\left(\frac{\partial S}{\partial V}\right)_P}{\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_A+\left(\frac{\partial T}{\partial V}\right)_P}\right]$$

It is given that,

$$\left(\frac{\partial P}{\partial V}\right)_A = \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial V}\right)_S$$

Hence, $$C_A = T\left[\frac{\left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_S + \left(\frac{\partial S}{\partial V}\right)_P}{\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_S + \left(\frac{\partial T}{\partial V}\right)_P}\right]$$

From reciprocity theorem, we can write,

$$\left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P \quad \text{and} \quad \left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$$

Substituting the above expressions, we get,

$$C_A = T \times \frac{\left(\frac{\partial S}{\partial P}\right)_V}{\left(\frac{\partial T}{\partial P}\right)_V} \times \frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial P}{\partial V}\right)_S}$$

Or, $$C_A = T\left(\frac{\partial S}{\partial T}\right)_A \times \frac{\text{isothermal elasticity}}{\text{adiabatic elasticity}}$$

Or, $$C_A = C_V\,\frac{C_V}{C_P} = \frac{{C_V}^2}{C_P}$$

Problem 16:

Compute the slopes of the vaporization and the sublimation curves for H_2O at 0˚C from the given data and show that they are two different lines and not two parts of the same line. Given the latent heat of vaporization is 607 cal and the latent heat of sublimation is 687 cal. Consider $V_g - V_l \approx V_g - V_s = 21 \times 10^4\ \text{cm}^3$

where V_g, V_l and V_s are volumes of the gas, liquid and solid states respectively.

Solution:

From the Clapeyron's equation,

$$\frac{dP}{dT} = \frac{\Delta \text{H}}{T(V_f - V_i)}$$

The slope of the vaporization curve at 0 ˚C is given by,

$$\frac{dP}{dT} = \frac{607 \times 4.2 \times 10^7}{273 \times 21 \times 10^4} = 0.337 \text{mm of Hg} / {}^\circ\text{C}$$

as, $V_g - V_l = 21 \times 10^4 \text{ cm}^3$

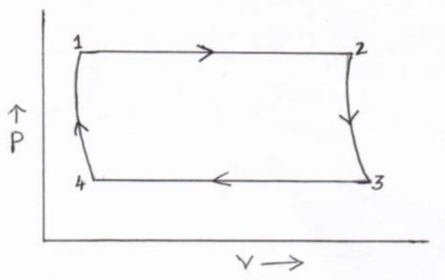
The slope of the sublimation curve at 0˚C is given by,

$$\frac{dP}{dT} = \frac{687 \times 4.2 \times 10^7}{273 \times 21 \times 10^4} = 0.381 \text{mm of Hg} / {}^\circ\text{C}$$

The sublimation curve is thus steeper than the vaporization curve at 0 ˚C temperature, so they are two different lines and not the two parts of the same line.

Problem 17:

Find the thermal efficiency of a reversible engine operating in a cycle consisting of two isotherms and two isobars, using ideal gas as working substance. Assume the specific heats C_p and C_v to be constant throughout the process.



Solution:

The thermal efficiency,

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$Q_1 = C_P(T_1 - T_2) + RT_1 \ln\frac{V_3}{V_2}$$

$$Q_1 = C_P(T_1 - T_2) + RT_1 \ln\frac{P_1}{P_2}$$

as, $P_1V_2 = P_2V_3$. Similarly,

$$Q_2 = C_P(T_1 - T_2) + RT_2 \ln\frac{V_4}{V_1}$$

$$Q_2 = C_P(T_1 - T_2) + RT_2 \ln\frac{P_1}{P_2}$$

$$\eta = 1 - \frac{C_P(T_1 - T_2) + RT_2 \ln\frac{P_1}{P_2}}{C_P(T_1 - T_2) + RT_1 \ln\frac{P_1}{P_2}}$$

$$\eta = \frac{R(T_1 - T_2)\ln\frac{P_1}{P_2}}{C_P(T_1 - T_2) + RT_1 \ln\frac{P_1}{P_2}}$$

Problem 18:

1 mole of O_2 escapes adiabatically into an evaporated chamber of such size that its final volume is 10 times to that of initial volume. Given that $C_v = 4.90$ cal and 'a' for oxygen is 1.36 atm lit^2 mol^{-2}. Calculate ΔS if the initial temperature is 0 ˚C. [For volume calculation use ideal gas equation.]

Solution:

It is an example of free expansion.

The initial volume of the gas O_2,

$$V = V_1 = \frac{nRT}{P} = \frac{1\text{ mole} \times 0.08206\text{ l atm K}^{-1} \times 273\text{ K}}{1\text{ atm}}$$

Or, $$V = 22.4\text{ L}$$

Now, we know that,

$$\int\left(\frac{\partial P}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \frac{a}{V^2}\,dV = a\frac{V_2 - V_1}{V_1 V_2} = a\frac{9V}{10V^2} = \frac{1.36 \times 9}{10 \times 22.4}\, l\text{ atm}$$

Again

$$\Delta \text{U} = nC_V(T_1 - T_2) - \frac{1.36 \times 9}{10 \times 22.4} \times 24.21\text{ cal}$$

The given problem is an example of adiabatic and free expansion.

So, q = 0 and w = 0 which gives ΔU = 0.

Hence we can write,

$$nC_V(T_1 - T_2) - \frac{1.36 \times 9}{10 \times 22.4} \times 24.21 = 0$$

Since, T_1 = 0 ˚C = 273 K,

we get T_2 = 272.73 K.

The value of entropy change for this process is

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Or, $\Delta S = 4.9 \ln \frac{272.73}{273} + 4.575 = 4.57 calK^{-1} = 19.12 JK^{-1}$