

## QUESTION#1

Answer:

The Gibbs free energy in terms of chemical potential:

The following is the relation between the Gibbs free energy and the chemical potential

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = N \left(\frac{\partial \mu}{\partial P}\right)_{T,N}$$

We also have,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN = -SdT + VdP + \mu dN$$

so that

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V.$$

Using this relation in Eq. (130) proves the second identity in (129). To prove the first relation in triple product identity,

$$\left(\frac{\partial P}{\partial T}\right)_{\mu,N} \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \left(\frac{\partial T}{\partial \mu}\right)_{P,N} = -1.$$

From Eq. (134) and  $G = \mu N$ , we have,

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N} = N \left(\frac{\partial \mu}{\partial T}\right)_{P,N}$$

And using these relations

$$G_A^{\text{soln}} = n_A \mu_A, G_B^{\text{soln}} = n_B \mu_B, \text{ etc.}$$

and, dividing by  $n_A, n_B$ , etc.

$$\frac{G_A^{\text{soln}}}{n_A} = \mu_A = \mu_A^0 + RT \ln X_A,$$

$$\frac{G_B^{\text{soln}}}{n_B} = \mu_B = \mu_B^0 + RT \ln X_B$$

Showing that 
$$\mu = \frac{G}{N} = \frac{1}{N}(A + pV)$$

## QUESTION# 2

Answer:

If we have a mixture of two substances present, the internal energy and all the other thermodynamical potentials will depend on how much of each is present, since there will be interactions between the molecules of each.

Here we focus on the Gibbs free energy, since the relevant conditions are usually those of fixed temperature and pressure.

We have  $G = G(T, P, N_1, N_2)$  where  $N_1$  and  $N_2$  are the number of molecules of each substance. (This is easily generalised more than two components.) So

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, N_1, N_2} dT + \left( \frac{\partial G}{\partial P} \right)_{T, N_1, N_2} dP + \left( \frac{\partial G}{\partial N_1} \right)_{T, P, N_2} dN_1 + \left( \frac{\partial G}{\partial N_2} \right)_{T, P, N_1} dN_2$$

Now the first two partial derivatives are  $-S$  and  $V$  as before. We *define*

$$\mu_1 = \left( \frac{\partial G}{\partial N_1} \right)_{T, P, N_2} \quad \text{and} \quad \mu_2 = \left( \frac{\partial G}{\partial N_2} \right)_{T, P, N_1}$$

giving

$$dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2$$

$\mu_1$  is called the **chemical potential** of substance 1. But what is its significance?

First, imagine only **one** substance present. Then

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T, P}$$

But  $G$  is extensive, and  $P$  and  $T$  are intensive, so  $G$  must be directly proportional to  $N$ :  $G(T, P, N) = Ng(T, P)$  (where  $g$  is the Gibbs free energy per molecule), and so  $\mu = g$ .

## QUESTION # 3

Answer:

At a given temperature the order of the translational partition function assuming volume and temperature are identical is

$$H_2 < HD < D_2$$

So the  $H_2$  has the largest translational potential value and almost same is in the case of partition function at a given temperature.

#### QUESTION # 4

Answer:

Expression for the enthalpy of vdW gas

$$\Delta H = -\mu C_p \Delta P + C_p \Delta T$$

Since for VDW gas

$$\mu C_p = 2aRT - b$$

The equation for  $\Delta H$

$\Delta H$  for a van der Waals gas should be:

$$\Delta H = C_p^{IG} \Delta T - 2a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) + b \left( \frac{RT_2}{V_2 - b} - \frac{RT_1}{V_1 - b} \right)$$

where  $C_p^{IG}$  is the heat capacity of the gas in the Ideal Gas (IG) region (low pressures and high specific volumes). For constant temperature ( $T_1 = T_2 = T$ ), this equation reduces to:

$$\Delta H = -2a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) + bRT \left( \frac{1}{V_2 - b} - \frac{1}{V_1 - b} \right)$$

#### QUESTION# 5

Answer:

- (a) Many aerospace applications (compression and expansion) involve flow of gases (e.g., air) and we thus examine the entropy relations for ideal gas behavior. The starting point is form of the combined first and second law,

$$du = Tds - Pdv.$$

For an ideal gas,  $du = c_v dT$ . Thus

$$Tds = c_v dT + Pdv \quad \text{or} \quad ds = c_v \frac{dT}{T} + \frac{P}{T} dv.$$

Using the equation of state for an ideal gas ( $Pv = RT$ ), we can write the entropy change as an expression with only exact differentials:

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}. \quad (a)$$

We can think of Equation (a) as relating the fractional change in temperature to the fractional change of volume, with scale factors  $c_v$  and  $R$ ; if the volume increases without a proportionate decrease in temperature (as in the case of an adiabatic free expansion), then  $s$  increases. Integrating Equation (a) between two states "1" and "2":

$$\Delta s = s_2 - s_1 = \int_{T_1}^{T_2} c_v \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}.$$

For a perfect gas with constant specific heats

$$\Delta s = s_2 - s_1 = c_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right).$$

In non-dimensional form (using  $R/c_v = (\gamma - 1)$ )

$$\frac{\Delta s}{c_v} = \ln \left( \frac{T_2}{T_1} \right) + (\gamma - 1) \ln \left( \frac{v_2}{v_1} \right), \quad \text{Entropy change of a perfect gas.} \quad (b)$$

Equation b is in terms of specific quantities. For  $N$  moles of gas,

$$\frac{\Delta S}{C_v} = N \left[ \ln \left( \frac{T_2}{T_1} \right) + (\gamma - 1) \ln \left( \frac{V_2}{V_1} \right) \right].$$

This expression gives entropy change in terms of temperature and volume. We can develop an alternative form in terms of pressure and volume, which allows us to examine an assumption we have used. The ideal gas equation of state can be written as

$$\ln P + \ln v = \ln R + \ln T.$$

Taking differentials of both sides yields

$$\frac{dP}{P} + \frac{dv}{v} = \frac{dT}{T}.$$

Using the above equation in Eq. (a), and making use of the

relations  $c_p = c_v + R$  ;  $c_p/c_v = \gamma$  , we find

$$ds = c_v \left[ \frac{dP}{P} + \frac{dv}{v} \right] + R \frac{dv}{v},$$

or

$$\frac{ds}{c_v} = \frac{dP}{P} + \gamma \frac{dv}{v}.$$

Integrating between two states 1 and 2

$$\frac{\Delta s}{c_v} = \ln \left( \frac{P_2}{P_1} \right) + \gamma \ln \left( \frac{v_2}{v_1} \right) = \ln \left[ \frac{P_2}{P_1} \left( \frac{v_2}{v_1} \right)^\gamma \right]. \quad (c)$$

The above equation is the entropy equation of ideal gas

### Question #5

(a) Expression for the entropy of a monoatomic ideal gas:  
many aerospace

(b)  $\Delta S = N K_B \ln P_1 / P_2$

The entropy of monoatomic ideal gas can be expressed in a famous equation called Sackur-Tetrode equation

$$S = N K \left[ \ln \left( \frac{V}{N} \left( \frac{4 \pi m U}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

where

$N$  = # of atoms (avogadro's #)

$K$  = Boltzmann's constant

$V$  = Volume

$U$  = Internal Energy

$h$  = Planck's constant

One of the thing which can be determined directly from this equation where  $N$  and  $U$  are constant ( $Q = W$ ) Expanding entropy expression for  $V_f$  and  $V_i$  with log combination rules leads to

$$\Delta S = N K \ln \frac{V_f}{V_i}$$

$$S = \frac{3}{2} N K \ln U + N K \ln V + N K \left[ \ln \left( \frac{1}{N} \left( \frac{4 \pi m}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

The temperature in terms of entropy

$$\frac{\partial S}{\partial U} = \frac{3}{2} \frac{N K}{U} \quad ; \quad T = \frac{1}{\partial S / \partial U} = \frac{2U}{3 N K}$$

This gives an expression for internal energy that is consistent with energy

$$U = \frac{3}{2} N K T$$

with  $kT/2$  of energy

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

$$\Delta S = \int_A^B \frac{dQ}{T} = \int_A^B \frac{dU + PdV}{T}$$

$$\Delta S = \int_A^B \frac{n C_v dT}{T} + \int_A^B \frac{nR dV}{V}$$

$$\Delta S = n C_v \ln \frac{T_B}{T_A} + nR \ln \frac{V_B}{V_A}$$

and

$$\frac{T_B}{T_A} = \frac{P_B V_B}{P_A V_A}$$

$$\text{Then } \ln \frac{T_B}{T_A} = \ln \frac{P_B}{P_A} + \ln \frac{V_B}{V_A}$$

as given that temperature is constant

so

$$\ln \frac{T_B}{T_A} = \ln \frac{P_B}{P_A} + \ln \frac{V_B}{V_A}$$

$$\ln \frac{V_B}{V_A} = -\ln \frac{P_B}{P_A} = \ln \frac{P_A}{P_B}$$

and

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\text{Initially } P_i = P_A = P_i$$

$$\text{Finally } P_f = P_B = P_f$$

so

$$\Delta S = nR \ln \frac{P_i}{P_f}$$