Diffusion in Multicomponent Solids
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Lecture - 05
Third law of Thermodynamics & Numerical Examples

Today let us go over couple of problems. The first problem deals with evaluation of Gibbs free energy, enthalpies and entropies of a substance based upon the knowledge of heat capacities at constant pressure and second problem deals with calculation of entropy changes associated with the irreversible process of heat transfer.

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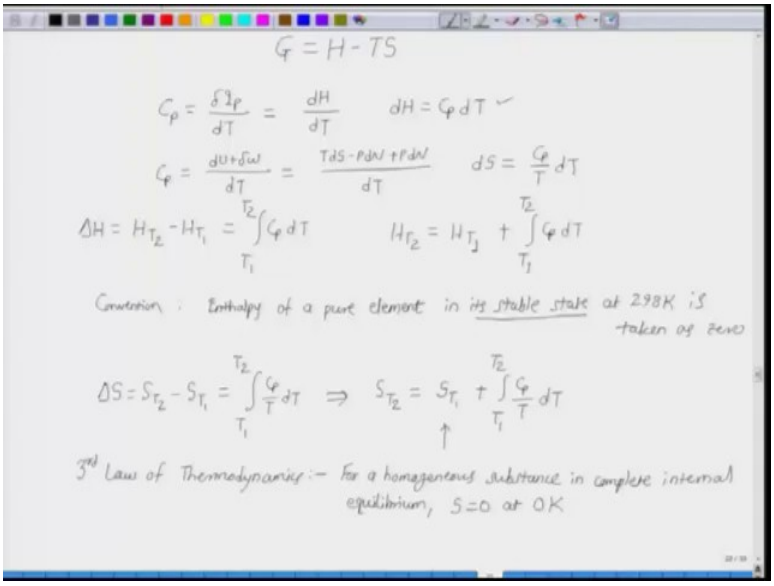

$$G = H - TS$$

$$C_p = \frac{\delta q_p}{dT} = \frac{dH}{dT} \qquad dH = C_p\, dT \checkmark$$

$$C_p = \frac{dU + \delta w}{dT} = \frac{TdS - PdV + PdV}{dT} \qquad dS = \frac{C_p}{T} dT$$

$$\Delta H = H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p\, dT \qquad H_{T_2} = H_{T_1} + \int_{T_1}^{T_2} C_p\, dT$$

Convention : Enthalpy of a pure element in its stable state at 298K is taken as zero

$$\Delta S = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p}{T} dT \Rightarrow S_{T_2} = \underset{\uparrow}{S_{T_1}} + \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

3rd Law of Thermodynamics:- For a homogeneous substance in complete internal equilibrium, S=0 at 0K

We have seen Gibbs free energy is a state function and it can be expressed as:

$$G = H - TS$$

We can use Gibbs free energy as a criteria for equilibrium with temperature and pressure as the independent variables. But, how to evaluate these Gibbs free energies? Basically we need to evaluate the enthalpies and entropies from which we can evaluate the Gibbs free energies. How do we get to enthalpies and entropies of a substance?

Here the heat capacity comes quite useful. We know that the heat capacity at constant pressure is defined as heat absorbed at constant pressure per unit rise in temperature.

$$C_P = \frac{\delta q_p}{dT}$$

Note that small heat effects are denoted by δq because heat is a path function and we are denoting small differences in temperature by dT because T is a state function, so we can define the exact differential.

Now we know that heat absorbed at constant pressure is basically the change in enthalpy. We can write this as:

$\delta q_p = dH$

$$C_P = \frac{dH}{dT}$$

Basically,

$$dH = C_P dT$$

Similarly, in order to get to entropy we can use the first law of thermodynamics. δq_p can be replaced by:

$$\delta q_p = dU + \delta w$$

i.e., change in internal energy plus work done and dU can be replaced by the combination of first and second law. We know:

$$dU = TdS - PdV$$

$$\delta w = PdV$$

Using these equations:

$$C_P = \frac{TdS}{dT}$$

Or,

$$dS = \frac{C_P}{T} dT$$

Let us get first to the enthalpy. If we make a state change and temperature of the first state is T_1 and the second state is T_2 then we can write ΔH for the state change as:

$$\Delta H = H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_P \, dT$$

To get to the enthalpy at any temperature T_2, we need to know enthalpy at one temperature T_1 and knowledge of C_P as a function of temperature:

$$H_{T_2} = H_{T_1} + \int_{T_1}^{T_2} C_P \, dT$$

Typically C_P are measurable quantities because we can measure the heat effects and there are databases available for C_P as a function of temperature over the different ranges of temperature for different materials. From there we can evaluate the integral $\int_{T_1}^{T_2} C_P \, dT$. But, what about enthalpy at temperature T_1? As I said in last class, we cannot evaluate the absolute quantities like enthalpies and Gibbs free energies. But it is sufficient to know the differences in these properties while going from one state to the other.

In other words we can use enthalpy at one temperature as a reference point and then we can evaluate the enthalpies with respect to that reference. Typically the convention for enthalpy is - the enthalpy of a pure element in its stable state at 298 Kelvin is taken as 0. By this convention, that is taken as the reference state for enthalpy evaluation.

For example, we know that iron at room temperature at 298 Kelvin exist as bcc. Enthalpy of bcc iron at 298 Kelvin is taken as 0. But, enthalpy of FCC iron at 298 Kelvin will obviously have some non-zero value. Then for entropy, we can write:

$$\Delta S = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_P}{T} \, dT.$$

$$S_{T_2} = S_{T_1} + \int_{T_1}^{T_2} \frac{C_P}{T} \, dT$$

What about the reference for entropy? Here we use the third law of thermodynamics. What is the third law?

Student: Entropy of a pure substance at zero Kelvin is zero.

Professor: The entropy of a homogeneous substance in complete internal equilibrium is 0 at 0 Kelvin. That is the third law of thermodynamics. This is important - the substance has to be in complete internal equilibrium. For example, as any crystalline solid has some equilibrium vacancy concentration at any temperature above 0 Kelvin and it is a function of temperature, vacancy concentration increases as the temperature increases. As you decrease the temperature, vacancy concentration should decrease with the temperature and at 0 Kelvin, the vacancy concentration should reach 0. But, this does not usually happen. The excess vacancies have to be annihilated at the sinks and as you cool down the kinetics become very slow and the vacancy concentration cannot approach equilibrium vacancy concentration at lower temperature. If you could reach 0 Kelvin, you would still have some vacancy excess left over and for that solid, then the entropy at 0 Kelvin will not be 0.

We assume basically that at 0 Kelvin there will be a pure crystalline solid without any defects. Entropy can have absolute values, evaluated based upon the third law of thermodynamics. There are data tabulated for standard entropies at 298 Kelvin. Based upon knowledge of C_P versus temperature we can get to the enthalpies and entropies and then from it we can evaluate the Gibbs free energies.

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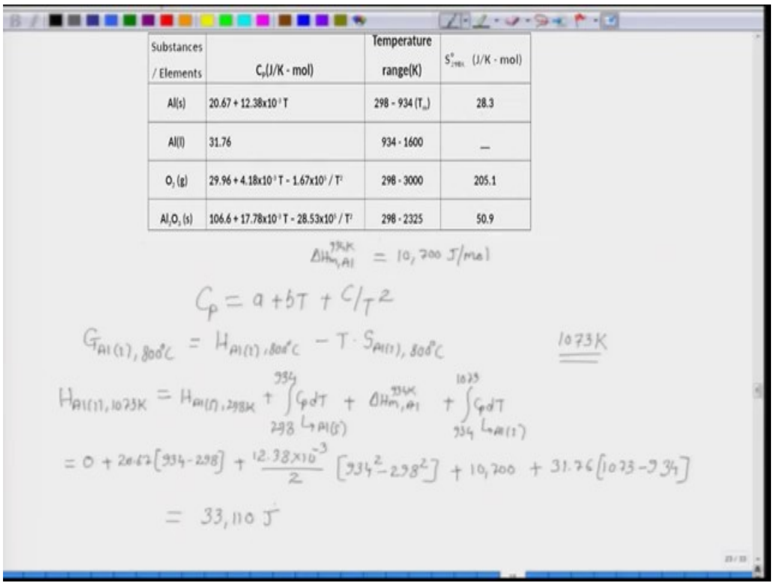

Substances / Elements	C_p(J/K - mol)	Temperature range(K)	S°_{298K} (J/K - mol)
Al(s)	$20.67 + 12.38\times10^{-3}T$	298 - 934 (T_m)	28.3
Al(l)	31.76	934 - 1600	–
O_2 (g)	$29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}/T^2$	298 - 3000	205.1
Al_2O_3 (s)	$106.6 + 17.78\times10^{-3}T - 28.53\times10^{5}/T^2$	298 - 2325	50.9

$$\Delta H^{934K}_{m,Al} = 10,700 \text{ J/mol}$$

$$C_p = a + bT + C/T^2$$

$$G_{Al(l),800^\circ C} = H_{Al(l),800^\circ C} - T \cdot S_{Al(l),800^\circ C} \qquad \underline{\underline{1073K}}$$

$$H_{Al(l),1073K} = H_{Al(l),298K} + \int_{298}^{934} \underbrace{C_p}_{Al(s)} dT + \Delta H^{934K}_{m,Al} + \int_{934}^{1073} \underbrace{C_p}_{Al(l)} dT$$

$$= 0 + 20.67[934-298] + \frac{12.38\times10^{-3}}{2}[934^2-298^2] + 10,700 + 31.76[1073-934]$$

$$= 33,110 \text{ J}$$

This C_P is typically expressed as a function of temperature. The empirical formula in the tabulated data usually is:

$$C_P = a + bT + \frac{C}{T^2}$$

For example, I have listed C_P's for some of the materials. You can see for solid aluminium the heat capacity is:

$$C_P = 20.67 + 12.38 \times 10^{-3} T$$

$$a = 20.67\ , b = 12.38$$

For oxygen gas,

$$a = 29.96\ , b = 4.18 \times 10^{-3} \text{ and } c = 1.67 \times 10^{-5}.$$

Based upon this let us say, if you want to evaluate Gibbs free energy of one mole of aluminium at let us say 800 ℃. That should be:

$$G_{Al(l),800\,℃} = H_{Al(l),800\,℃} - T\,S_{Al(l),800\,℃}$$

800 ℃is basically 1073 Kelvin. If we have to write the formula for enthalpy of aluminium liquid at 1073 Kelvin then how do we go about this?

$$H_{Al(l),1073\,K} = H_{Al(s),298\,K} + \int_{298}^{934} C_{P,Al(s)}\,dT + \Delta H_m + \int_{934}^{1073} C_{P,Al(l)}\,dT$$

We know that the enthalpy of solid aluminium at 298 Kelvin is by convention 0. We know H of solid aluminium at 298 Kelvin and we know how the C_P of solid aluminium varies with temperature. Aluminium will melt in between before we reach 1073 Kelvin. It melts at 934 Kelvin. So we can use C_P solid only up to 934 Kelvin. Then when aluminium melts it will absorb heat, so we need to consider the latent heat of melting, ΔH_m of aluminium at 934 Kelvin. Then aluminium becomes liquid and we have to heat liquid aluminium from 934 to the temperature desired, that is, 1073 Kelvin. For this, we have to use C_P of liquid aluminium. The first integral C_P is for aluminium solid.

$$\Delta H_m = 10{,}700 \frac{J}{mole}$$

$$C_{P,Al(s)} = 20.67 + 12.38 \times 10^{-3} T$$

$$C_{P,Al(l)} = 31.76$$

$$H_{Al(l),1073\,K} = 0 + \frac{12.38\times10^{-3}}{2}\left(934^2 - 298^2\right) + 10,700 + 31.76\left(1073 - 934\right)$$

$$H_{Al(l),1073\,K} = 33,110\;Joules$$

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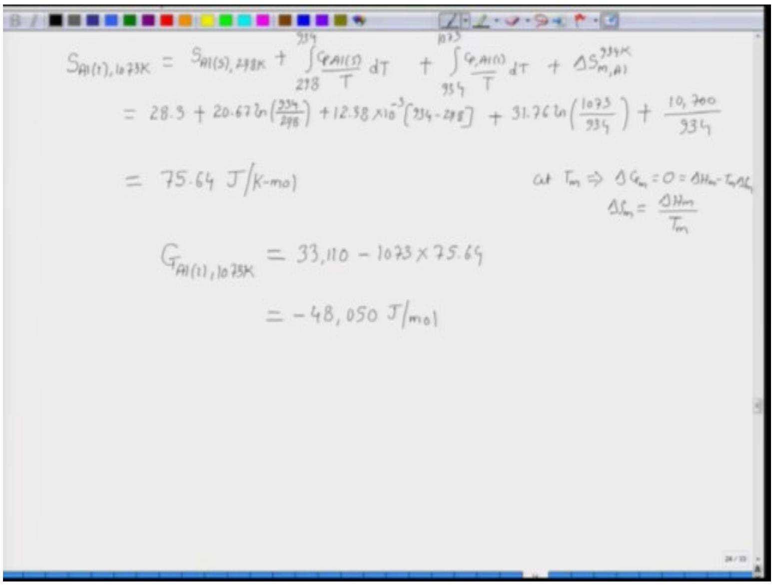

$$S_{Al(l),1073K} = S_{Al(s),298K} + \int_{298}^{934} \frac{C_{P,Al(s)}}{T}\,dT + \int_{934}^{1073} \frac{C_{P,Al(l)}}{T}\,dT + \Delta S_{m,Al}^{934K}$$

$$= 28.3 + 20.67\ln\left(\frac{934}{298}\right) + 12.38\times10^{-3}\left[934-298\right] + 31.76\ln\left(\frac{1073}{934}\right) + \frac{10,700}{934}$$

$$= 75.64\;J/K\text{-mol}$$

$$\text{at } T_m \Rightarrow \Delta G_m = 0 = \Delta H_m - T_m\Delta S_m$$

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

$$G_{Al(l),1073K} = 33,110 - 1073\times75.64$$

$$= -48,050\;J/mol$$

Now next we evaluate entropy. Entropy of liquid aluminium at 1073 Kelvin can be written as:

$$S_{Al(l),1073\,K} = S_{Al(s),298\,K} + \int_{298}^{934} \frac{C_{P,Al(s)}}{T}\,dT + \Delta S_{m,Al} + \int_{298}^{934} \frac{C_{P,Al(l)}}{T}\,dT$$

At 934 K, there is melting occurring. So we need to consider the entropy of melting of aluminium at the equilibrium melting point which is 934 Kelvin.

This is a tabulated data. We know:

$$S_{Al(s),298\,K} = 28.3\,\frac{J}{Kmole}$$

$$S_{Al(l),1073\,K} = 28.3 + \int_{298}^{934} \frac{20.67 + 12.38\times10^{-3}T}{T}\,dT + \Delta S_{m,Al} + \int_{298}^{934} \frac{31.76}{T}\,dT$$

Finally we need the entropy of melting. How do we get to this? We know the enthalpy of melting and at equilibrium melting temperature, we know $\Delta G_m = 0$. Because at equilibrium, melting solid is in equilibrium with liquid. If we change the state from solid to liquid, there should be no change in Gibbs free energy which we know is:

$$\Delta G_m = \Delta H_m - T_m \Delta S_m$$

At equilibrium melting temperature:

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

$$\Delta H_m = 10,700$$

So,

$$\Delta S_m = \frac{10,700}{934} = 75.64 \frac{J}{Kmole}$$

And once we know H and S we can know Gibbs free energy of liquid aluminium at 1073 Kelvin:

$$G_{Al(l),1073\,K} = 33,110 - 1073 \times 75.64 = 48,050 \frac{J}{m}$$

This is how we can get to the Gibbs free energies of the substances based upon the tabulated data of heat capacities at constant pressure. Heat capacity becomes a very useful parameter. It can be experimentally determined, tabulated and can be used to generate the Gibbs free energy data as a function of temperature. Any question?

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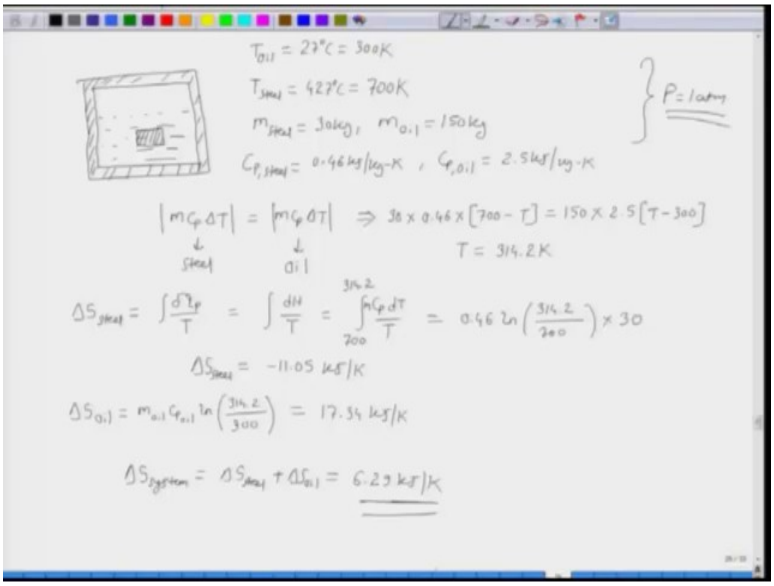

$T_{oil} = 27°C = 300K$

$T_{steel} = 427°C = 700K$

$m_{steel} = 30kg, \quad m_{oil} = 150kg$

$C_{P,steel} = 0.46 kJ/kg\text{-}K, \quad C_{P,oil} = 2.5 kJ/kg\text{-}K$

$\left.\right\} P = 1atm$

$$\underset{\text{steel}}{\underset{\downarrow}{|mC_P\Delta T|}} = \underset{\text{oil}}{\underset{\downarrow}{|mC_P\Delta T|}} \Rightarrow 30 \times 0.46 \times [700 - T] = 150 \times 2.5 [T - 300]$$

$$T = 314.2K$$

$$\Delta S_{steel} = \int \frac{\delta q_P}{T} = \int \frac{dH}{T} = \int_{700}^{314.2} \frac{mC_P dT}{T} = 0.46 \ln\left(\frac{314.2}{700}\right) \times 30$$

$$\Delta S_{steel} = -11.05 kJ/K$$

$$\Delta S_{oil} = m_{oil} C_{P,oil} \ln\left(\frac{314.2}{300}\right) = 17.34 kJ/K$$

$$\Delta S_{system} = \Delta S_{steel} + \Delta S_{oil} = \underline{\underline{6.29 kJ/K}}$$

Let us take a look at another problem. This is basically the problem of evaluating the changes in entropy when the heat transfer takes place obviously from hotter body to the colder body. This is an irreversible process. Suppose we have a container of oil which is at normal room temperature that is 27 $℃$ or 300 Kelvin and we drop a piece of steel in which was at 427 $℃$ (700 K) before dropping.

As soon as we drop the steel piece in the oil, there will be heat transfer from steel piece to the oil. The temperature of steel will come down, temperature of oil will increase and the heat transfer will continue until the equilibrium state is reached. And what is equilibrium state? The equilibrium state is when there is a uniform temperature of oil and steel. what is that temperature T? So, we first need to evaluate that temperature T.

We need to know the quantity of oil and steel of course. Let us say the mass of steel is 30 kg and mass of oil is 150 kg. Of course we need to know the C_P. C_P of steel is given as:

$$C_{P,Steel} = 0.46 \frac{kJ}{kgK}$$

And C_P of oil as:

$$C_{P,Oil} = 2.5 \frac{kJ}{kgK}$$

And this is all occurring at the constant pressure of one atmosphere. The change in entropy is what we need to calculate.

First we need to get at the final temperature of the system, the system of oil plus steel. Also, this container is given to be a perfectly insulated container which means there is no external heat effect. The heat is transferred between steel and oil but there is no external heat effect. How much heat transfer is occurring can be known based upon the $C_P$data. Whatever heat is lost by steel should be equal to the heat gained by the oil.

We can write:

$$(mC_P \Delta T)_{Steel} = (mC_P \Delta T)_{Oil}$$

Now we have to consider the magnitudes. We can write:

$$30 \times 0.46(700 - T) = 150 \times 2.5(T - 300)$$

On solving for T one obtains:

$$T = 314.2\, Kelvin$$

The final temperature of oil plus steel system will be 314.2 Kelvin. Now, let us evaluate the entropy change. For steel you can write,

$$\Delta S_{Steel} = \int \frac{\delta q_P}{T}$$

We know pressure is constant and δq_P is heat absorbed at constant pressure. That should be equal to:

$$\Delta S_{Steel} = \int \frac{dH}{T} = \int_{700}^{314.2} \frac{mC_P}{T} dT$$

We know the integral is from the initial temperature of steel which was 700 K to the final temperature which is 314.2 K.

$$C_{P,Steel} = 0.46$$

$$\Delta S_{Steel} = 30 \times 0.46 \ln\left(\frac{314.2}{700}\right)$$

There is a mass term in the entropy equation because C_P is given in terms of per kg. Obviously, 314 is less than 700 so this logarithm is negative or the entropy change for steel is negative.

$$\Delta S_{Steel} = -11.05 \frac{kJ}{K}$$

Negative value is obvious because steel is losing heat. So entropy has to decrease. There is no other external heat effect. Similarly, for oil we can write:

$$\Delta S_{Oil} = \int_{300}^{314.2} \frac{mC_P}{T} dT = 17.34 \frac{kJ}{K}$$

For oil obviously heat is being absorbed by oil, so there is an increase in entropy. And entropy change is positive.

If you consider oil plus steel as the system then we have:

$$\Delta S_{Steel} + \Delta S_{Oil} = -11.05 + 17.34 = 6.29 \frac{kJ}{K}$$

The net entropy change for the system is positive because it is adiabatic. The walls are given to be insulated, perfectly insulated at constant pressure.

Student: Extensive property… But when…

Professor: Temperature is an intensive property. Any question? Alright, we will stop here.

Keyword: Heat capacity at constant pressure, Reference state, Third law of thermodynamics