Thermal Physics

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Lecture - 50
Thermodynamics of Chemical Reaction

Hello and welcome back to the last lecture of week 10, on this NPTEL course on thermal physics. Now, in this week we have discussed about thermodynamic relations, we have discussed about free energy functions. We have used in the last lecture we have seen how free energy function can be I mean what is the significance of free energy function in attaining equilibrium under certain condition.

Now, today we will start this lecture by looking into one example, where a certain free energy function has to be optimized in order to get equilibrium.

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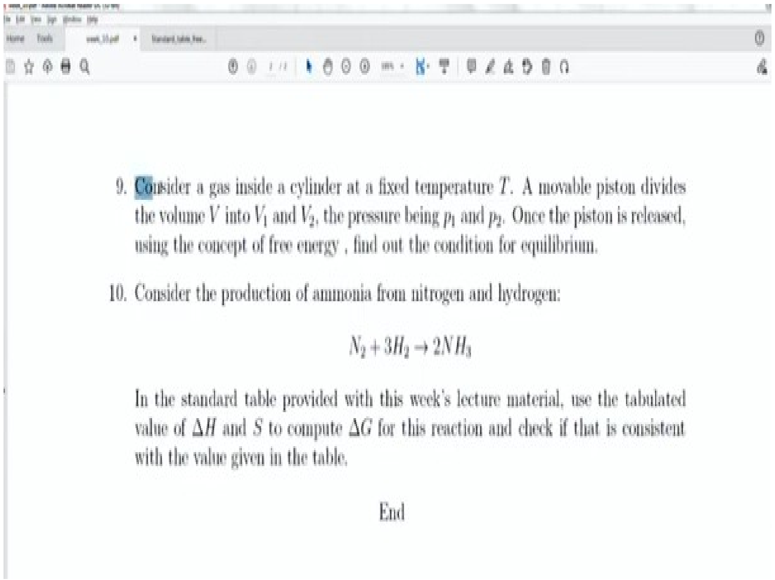

9. Consider a gas inside a cylinder at a fixed temperature T. A movable piston divides the volume V into V_1 and V_2, the pressure being p_1 and p_2. Once the piston is released, using the concept of free energy , find out the condition for equilibrium.

10. Consider the production of ammonia from nitrogen and hydrogen:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

In the standard table provided with this week's lecture material, use the tabulated value of ΔH and S to compute ΔG for this reaction and check if that is consistent with the value given in the table.

End

So, problem number nine of this week's problem set. Consider a gas inside a cylinder at a fixed temperature T. A movable piston divides the volume V into V 1 and V 2 the pressure being p 1 and p 2. Once the piston is released using the concept of free energy, find out the condition for equilibrium. Now, this is a problem where we have a fixed temperature T and the overall volume of the cylinder does not change.

So, it is a fixed temperature fixed volume scenario, of course this piston is free to move, so that the values of V 1 and V 2 will change.

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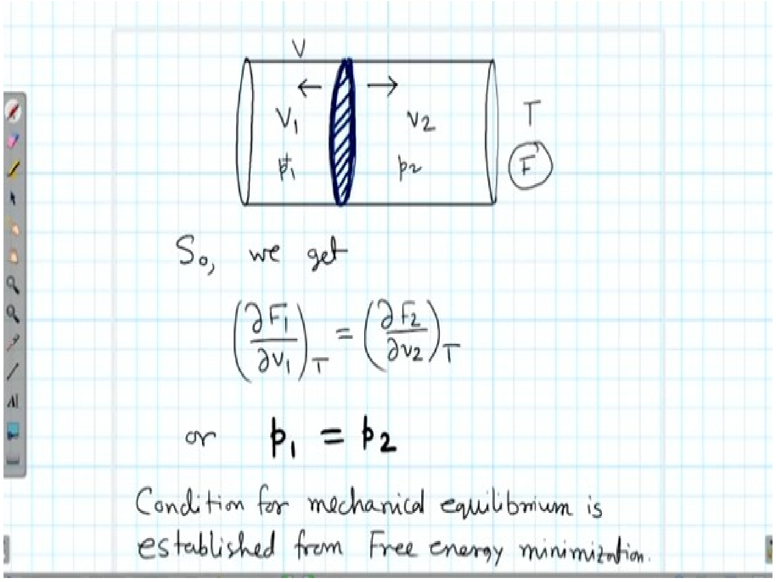

So, we get

$$\left(\frac{\partial F_1}{\partial V_1}\right)_T = \left(\frac{\partial F_2}{\partial V_2}\right)_T$$

or $p_1 = p_2$

Condition for mechanical equilibrium is established from Free energy minimization.

So, unfortunately, I just put this diagram in the second page, so but I hope you understand. So, this is the situation this overall volume V of this cylinder is fixed. Temperature T is also fixed, so this is the system with fixed temperature and volume. Now, which free energy has to be optimized in order to get the equilibrium condition? That is F the Helmholtz free energy that has to be optimized.

So, the situation is like this, initially we have V 1 and V 2 and the pressure being p 1 and p 2. So, once we release the piston, it should move back and forth before it can go to equilibrium. Now, every movement will alter the values of V 1 and V 2.

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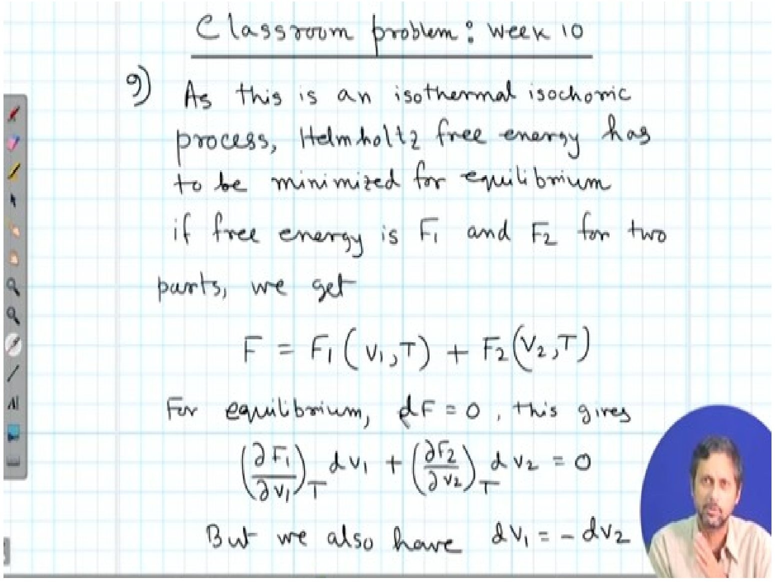

Classroom problem: week 10

9) As this is an isothermal isochoric process, Helmholtz free energy has to be minimized for equilibrium

if free energy is F_1 and F_2 for two parts, we get

$$F = F_1(V_1, T) + F_2(V_2, T)$$

For equilibrium, $dF = 0$, this gives

$$\left(\frac{\partial F_1}{\partial V_1}\right)_T dV_1 + \left(\frac{\partial F_2}{\partial V_2}\right)_T dV_2 = 0$$

But we also have $dV_1 = -dV_2$

So, let us write the free energy functions of this individual compartment as F 1 and F 2, and the total free energy F is F 1, which is a function of V 1, T and F 2 which is a function of V 2, T. So, for equilibrium dF should be equal to 0, assuming that these are all reversible processes; the movement of the piston is reversible. So, it can take dF is equal to 0. So, this gives you delta F1 d delta V 1 with fixed temperature is times dV 1 plus delta F 2 delta V 2 at fixed temperature times dV 2 is equal to 0.

But also, we have dV 1 is equal to minus dV 2. This is simply because; V = V 1 + V 2 which is a constant. So, that means dV 1 + dV 2 = 0 which directly leads to this particular condition. So, we have this once we put dV 1 = - dV 2 into this equation, then we get del F 1 del V 1 T is equal to del F 2 del V 2 T, which means p 1 = p 2. So, these are the first derivative of this free energy with respect to volume is nothing but pressure.

So, we have pressure of this side has to be equal to the pressure of this side. So, it does not matter, what are the values of V 1 and V 2. As long as the pressure in the two sides of the piston is equal, we should get equilibrium. And that is a very intuitive result, we do not actually need the concept of free energy for that. But we see that by optimizing the free energy function, we can directly get to this particular relation.

Now, so that means condition for mechanical equilibrium which is p 1 = p 2 is established from free energy minimization.

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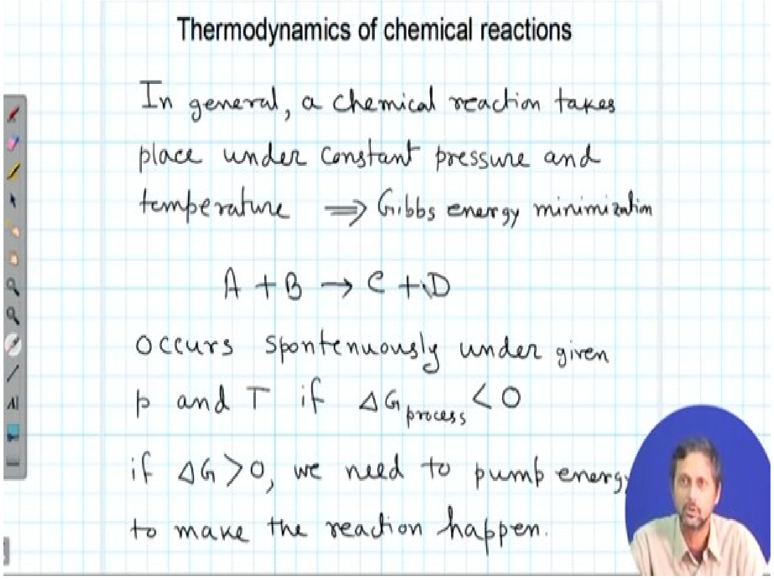

Thermodynamics of chemical reactions

In general, a chemical reaction takes place under constant pressure and temperature $\Rightarrow$ Gibbs energy minimization

$$A + B \rightarrow C + D$$

occurs spontenuously under given p and T if $\Delta G_{process} < 0$

if $\Delta G > 0$, we need to pump energy to make the reaction happen.

Now next what we are going to discuss is the thermodynamics of chemical reaction. A chemical reaction usually takes place as a fixed temperature and pressure. So, that means we can get the condition for a chemical or for such systems which has fixed temperature and pressure; we usually minimize Gibbs energy function. So, let us focus on this relation A plus B reaction that, where we have two compounds or two elements or rather, we should call it the two reactant actually.

A and B they combine to give the product C and D. Now, if this the final, the total Gibbs change in Gibbs free energy of this process is less than 0. Then this process will be a continuous process. Otherwise, we might need to put extra energy into it.

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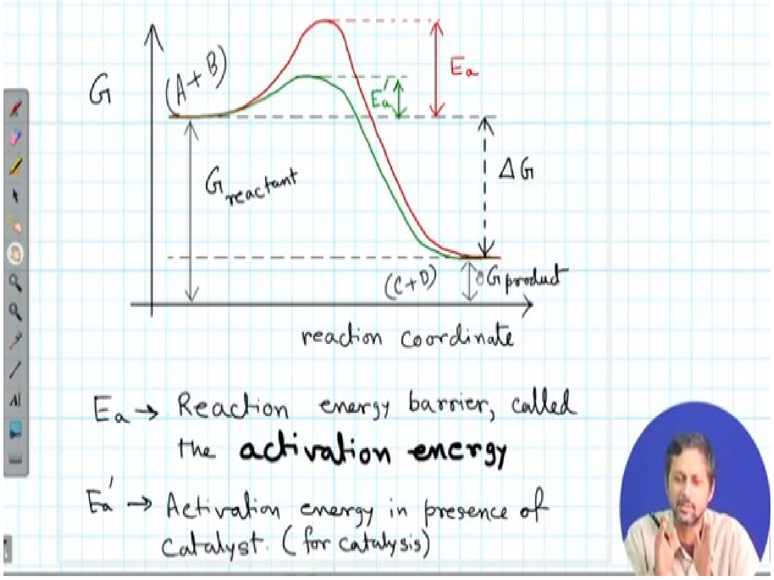

E_a → Reaction energy barrier, called the **activation energy**

E_a' → Activation energy in presence of catalyst. (for catalysis)

So, let us try to understand this pictorially, that will be easy for us to realize. So, here in this x, in this case the y axis, we just draw the Gibbs free energy of the system. And here we have certain reaction coordinate, reaction coordinate would be temperament time, could be some other parameter which is monitored during the reaction. But this means reaction is taking place along the positive of this coordinate. So, initially we have the products A and B.

So, the combination of them, actually this is a combination of them A plus B, which has a total Gibbs energy G of reactant. Now, this is measured with some zero level, arbitrary zero level, once again free energy, the absolute value of energy has to be measured from some arbitrary user defined zero level. Now, what happens is? This reaction is, once this reaction is complete, this is the product, where we have C plus D.

The total Gibbs energy has to be less than the systems gives energy has to be less than its initial point in order to have a spontaneous reaction from A plus B to C plus D. I mean, I am just saying A + B and C plus D, but it could be any reaction of any number of components, this is the general scheme. Also, we have to remember that, of course this is not exactly part of this discussion, but let me also introduce activation energy for you.

So, from here to here you might have to, you know there might not be a smooth path connecting these two, I mean, I should not say smooth but monotonically decreasing path connecting the initial and the final point. It might so happen that in between there is a maximization maximal point for certain reaction coordinate. There is a maximal value of the Gibbs energy and then it comes down to its lowest point.

So, that energy barrier has to be surmounted in order for this reaction to take place. This energy barrier height which has to be surmounted is called the activation energy of the reaction. Now, what happens is in certain reaction this activation energy is so high. So, that the rate of the reaction is very low. So, what we have to do is? We sometimes use catalysis. We have to use some catalyst.

What catalyst does is? It does not alter the initial and the final free energy of the system. So, the reactant and the product free energy difference remains the same, which is given by delta G, so delta G of the reaction does not change, but the barrier height comes down from A-to-A dash, which is less than A. So, this is more or less the pictorial, I mean this is how we can pictorially understand a reaction scheme.

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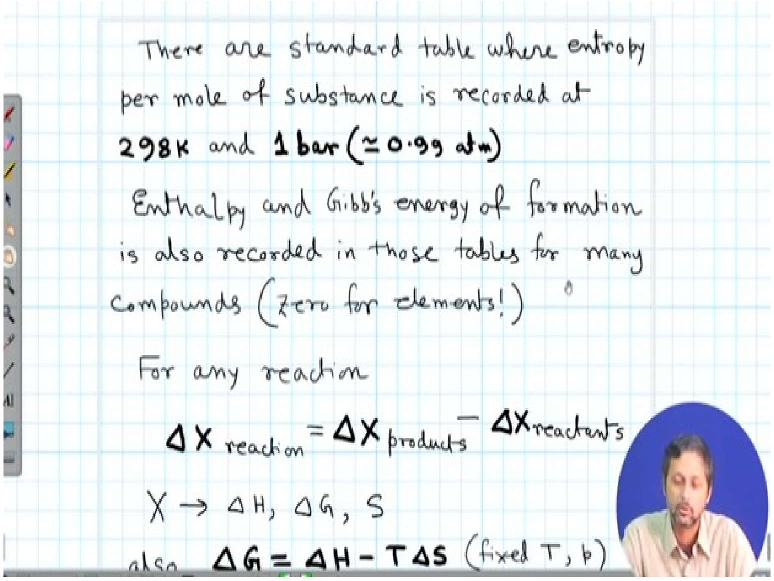

There are standard table where entropy per mole of substance is recorded at **298K** and **1 bar** ($\simeq 0.99$ atm)

Enthalpy and Gibb's energy of formation is also recorded in those tables for many compounds (zero for elements!)

For any reaction

$$\Delta X_{\text{reaction}} = \Delta X_{\text{products}} - \Delta X_{\text{reactants}}$$

$X \rightarrow \Delta H, \Delta G, S$

also $\Delta G = \Delta H - T\Delta S$ (fixed T, p)

So, to understand it better, so we need to know the values of such, you know the free energy function. Now, it so happens that there are standard table, where entropy for one mole of substance is recorded at 298 kelvin and 1 bar pressure, which is almost 0.99 atmosphere. So, enthalpy and Gibbs free energy of formation is also recorded for the compounds and for elements, it is the enthalpy and tree Gibbs free energy of formation is 0.

Now, for any of any reaction, if we have delta X, if we want to calculate delta X reaction, where X is either of Helmholtz change in Gibbs enthalpy or Gibbs free energy or, delta X reaction is equal to delta X product minus delta X reactant. Also, we have to remember this very important relation that delta G is equal to delta H minus T dS at fixed temperature, T delta S in fixed temperature and pressure.

So, using these two simple relation or simple equation, we can actually calculate the reaction, we can actually compute the change in Gibbs free energy or any other important parameter for a chemical reaction.

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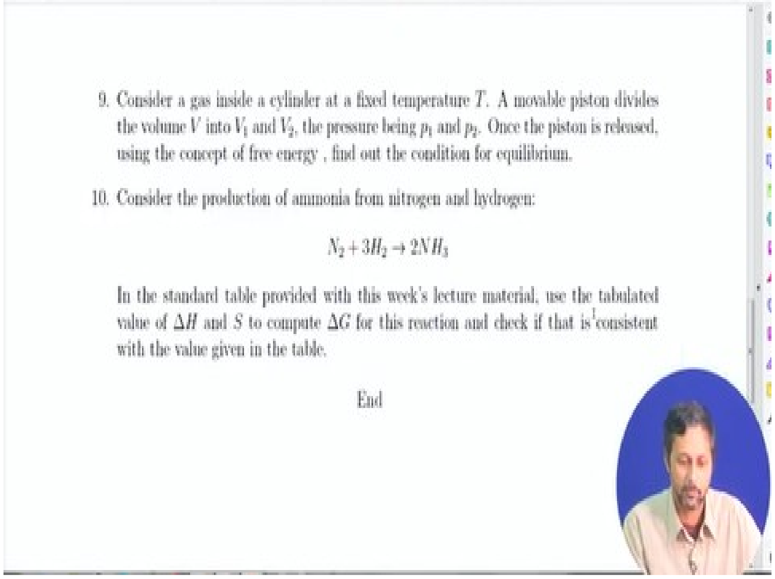

9. Consider a gas inside a cylinder at a fixed temperature T. A movable piston divides the volume V into V_1 and V_2, the pressure being p_1 and p_2. Once the piston is released, using the concept of free energy , find out the condition for equilibrium.

10. Consider the production of ammonia from nitrogen and hydrogen:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

In the standard table provided with this week's lecture material, use the tabulated value of ΔH and S to compute ΔG for this reaction and check if that is consistent with the value given in the table.

End

So, let us take one example; consider the production of ammonia from nitrogen and hydrogen by this reaction, N 2 plus 3H 2 is equal to 2NH 3. In the standard table provided with this week's lecture material; please check that these have been provided in the website. Use the tabulated values of delta H and S to compute delta G for this reaction and check if that is consistent with the values given in the table.

Now, it so happens that delta S can be directly measured from the specific heat data for which is available for almost all the elements and many, many compounds. Similarly, delta H is the formation in the enthalpy of formation, which is 0 for any element, but non-zero for compounds. In certain compound which takes place, which is formed in a spontaneous reaction, delta H will be negative. In certain cases where energy has to be put in, we have delta H to be positive.

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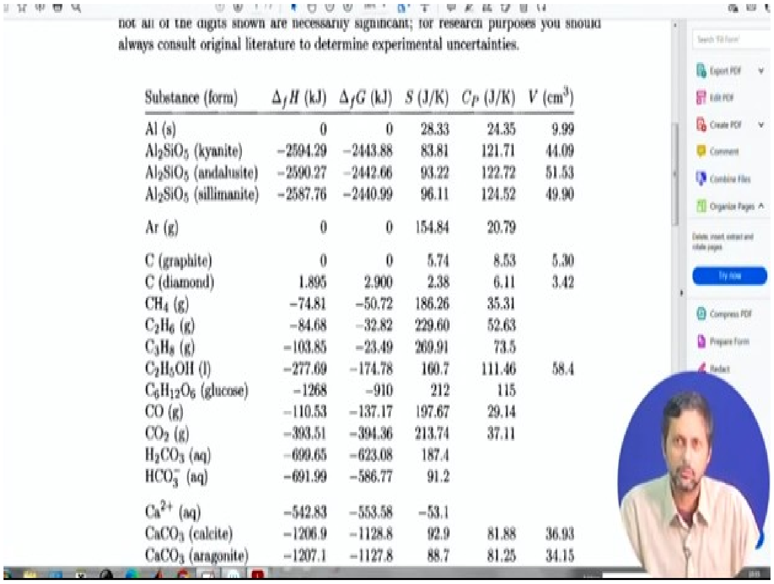

not all of the digits shown are necessarily significant; for research purposes you should always consult original literature to determine experimental uncertainties.

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
Al (s)	0	0	28.33	24.35	9.99
Al_2SiO_5 (kyanite)	−2594.29	−2443.88	83.81	121.71	44.09
Al_2SiO_5 (andalusite)	−2590.27	−2442.66	93.22	122.72	51.53
Al_2SiO_5 (sillimanite)	−2587.76	−2440.99	96.11	124.52	49.90
Ar (g)	0	0	154.84	20.79	
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)	1.895	2.900	2.38	6.11	3.42
CH_4 (g)	−74.81	−50.72	186.26	35.31	
C_2H_6 (g)	−84.68	−32.82	229.60	52.63	
C_3H_8 (g)	−103.85	−23.49	269.91	73.5	
C_2H_5OH (l)	−277.69	−174.78	160.7	111.46	58.4
$C_6H_{12}O_6$ (glucose)	−1268	−910	212	115	
CO (g)	−110.53	−137.17	197.67	29.14	
CO_2 (g)	−393.51	−394.36	213.74	37.11	
H_2CO_3 (aq)	−699.65	−623.08	187.4		
HCO_3^- (aq)	−691.99	−586.77	91.2		
Ca^{2+} (aq)	−542.83	−553.58	−53.1		
$CaCO_3$ (calcite)	−1206.9	−1128.8	92.9	81.88	36.93
$CaCO_3$ (aragonite)	−1207.1	−1127.8	88.7	81.25	34.15

So, I should not say all elements it is 0, for example if we look at the standard table, so this is these looks something like this we have delta H which is enthalpy of formation, delta G del S C p and V. So, V is the specific volume and this is all for one mole of the substance under 1.99 atmosphere pressure and 28 degree or 25 degree centigrade. This is not a full table, which I have taken adapted from one text book.

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This is only very few elements and compounds here, but the actual standard table will be lot more, but we do not need that for our purpose, because primarily we are not dealing much about with reaction kinetics.

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So, let us look at the standard table, for example as I was trying to tell you, for hydrogen gas H 2, gas enthalpy of formation is 0, enthalpy Gibbs energy of formation is 0, entropy is 130.68 joules per kelvin. Also, one thing please note that enthalpy of formation and Gibbs free energy is given in kilojoules, whereas the entropy of formation is given in joules per kelvin. So, some unit conversion might be necessary.

Now, if we look at the elemental hydrogen here, what do we get? We get an enthalpy of formation of 217.97 kilojoules, that means in order to break two moles of, I mean the hydrogen gas, and produce one mole of atomic hydrogen we need to have 217.97 kilo joules of energy under normal fixed pressure and temperature. So, this is the significance of this. Similarly, H 2 O which we will be discussing very soon, has an enthalpy of formation of minus 285.8.

There almost to minus 286 kilo joules that means one mole of height. If we have one mole of hydrogen gas and half mole of oxygen gas, they will continuously react they will release energy of 286 kilojoules per mole to produce one mole of water. So, this is how we read the table.

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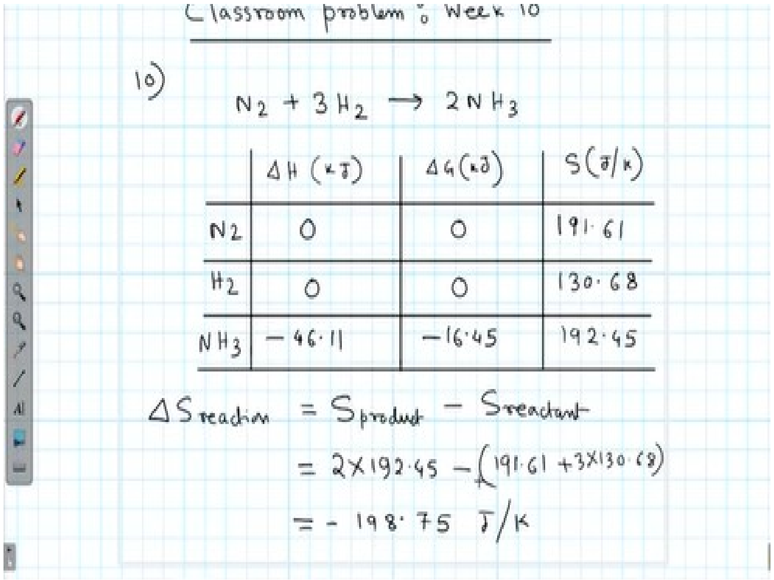

Classroom problem : Week 10

10) $N_2 + 3H_2 \rightarrow 2NH_3$

	ΔH (kJ)	ΔG (kJ)	S (J/K)
N_2	0	0	191.61
H_2	0	0	130.68
NH_3	−46.11	−16.45	192.45

$$\Delta S_{reaction} = S_{product} - S_{reactant}$$
$$= 2 \times 192.45 - (191.61 + 3 \times 130.68)$$
$$= -198.75 \ J/K$$

So, now let us focus on this particular reaction N 2 plus 3 H 2 is equal to 2 NH, I have already taken the data from here. The one point I was trying to tell you that enthalpy is something that can be directly measurable, because under constant pressure and temperature, the heat of reaction, the heat absorbed or heat generated during the reaction is the measure of enthalpy change. So, that is why delta G is delta H is measurable.

S is directly measured I mean calculated from the specific heat data, which is directly measurable and, delta G is calculated from these two. So, delta G is not directly measurable, but it is calculated from the change in delta H and S. So, let us verify whether these calculations, which are given in this table are accurate enough, that is exactly what we are supposed to do here. We have N 2 plus 3 H 2 is equal to 2 NH 3, we have delta H, delta G and S tabulated here.

For N 2 and H 2 these are 0, 0, 0, 0 both the free energies or both the energy functions. Entropy of course there exists some finite number for, sorry I should not say there exist, I mean there are some numbers given for reported for these two elements and one compound. Now, for ammonia the enthalpy of formation is minus 46.11 and Gibbs free energy of formation is - 16.45. This is what we need to verify. So, what we need to do is?

We need to first calculate delta S of reaction, which is S product minus S reactant. What is s product? Ammonia, so it is 2 moles of ammonia, so we put 2 into 192.45 and sorry, I missed the 3 here, it should be 3 into 130.68 plus 191.61 whole minus and this will give you 198.75 joules per Kelvin. So, delta S of reaction is minus almost minus 200 joules per kelvin. Now, the reaction is taking place, if it is not explicitly mentioned.

We have to assume that the reaction is taking place at 25 degree centigrade, that is the normal room temperature, where all these values have been tabulated.

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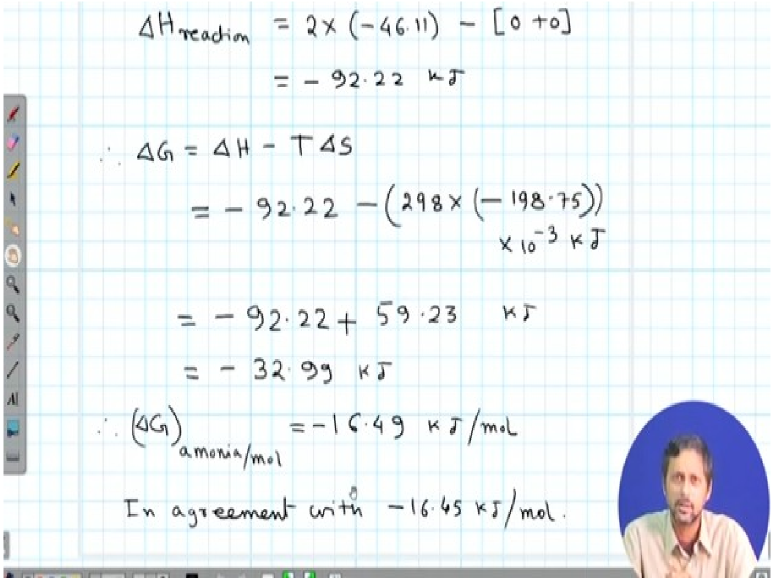

$$\Delta H_{reaction} = 2 \times (-46.11) - [0 + 0]$$

$$= -92.22 \text{ kJ}$$

$$\therefore \Delta G = \Delta H - T\Delta S$$

$$= -92.22 - (298 \times (-198.75)) \times 10^{-3} \text{ kJ}$$

$$= -92.22 + 59.23 \text{ kJ}$$

$$= -32.99 \text{ kJ}$$

$$\therefore (\Delta G)_{amonia/mol} = -16.49 \text{ kJ/mol}$$

In agreement with -16.45 kJ/mol.

So, delta H reaction is equal to, also we have to calculate the delta H reaction, which is once again the delta H of product minus delta H of reactant, delta H of products is 0 and 0, delta H of reactant is minus 46.11, product is minus 46.11, delta H of reactant is 0. So, we have delta H of reaction is minus 92.22 kilojoules. So, delta G which is delta H minus T delta S is equal to 92.22 minus T is 198, so we should put an extra bracket here. T is 298 delta S is minus 198.75.

And, this is once again please remember, this is given in joules per Kelvin, whereas the other quantities are kilojoules. So, we have to put a 10 to the power minus 3 to make it kilo joules. If we do this and simplify, we get 32.99 kilojoules. So, this is for the Gibbs energy of formation of two moles of ammonia, because a reaction produces two moles of ammonia here. So, if we want to compute for 1 mole, we have to divide it by 2 and we get minus 16.49 kilojoules per mole.

So, it is in general in agreement with the reported tabulated value of minus 16.45 kilojoules per mole. So, we get 16.49, this is 16.45. And of course, this is a spontaneous reaction, because the total change in Gibbs free energy is negative. So, why I chose this example? It is a rather easy problem. But let me tell you that typically in a physics course, we people do not teach this type of things. And reaction kinetics is a very important application of the free energy functions.

So, I thought, I will just take one example or I will have more examples coming actually, I will discuss this briefly. So, that you have a general idea on how to calculate or how the reaction kinetics work. A course on chemical thermodynamics will start from this place. So, the probably in the first or second lecture the instructor will introduce to chemical kinetics or the free energy function and the change in free energy function during a chemical reaction.

Also, there is more advanced technique to calculate the chemical, I mean look into the chemical kinetics starting from this free energy function, we are not going into those things.

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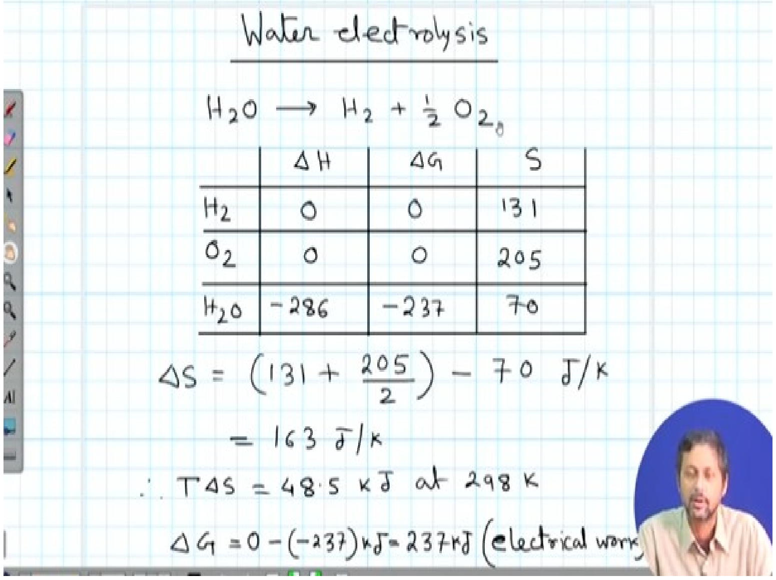

Water electrolysis

$H_2O \longrightarrow H_2 + \frac{1}{2} O_{2g}$

	ΔH	ΔG	S
H_2	0	0	131
O_2	0	0	205
H_2O	−286	−237	70

$\Delta S = \left(131 + \frac{205}{2}\right) - 70 \text{ J/K}$

$= 163 \text{ J/K}$

$\therefore T\Delta S = 48.5 \text{ kJ at } 298 \text{ K}$

$\Delta G = 0 - (-237) \text{ kJ} = 237 \text{ kJ}$ (electrical work

So, let me take another example. Another very important and very well studied system is water electrolysis. Water as we all know, if we put two electrodes inside water, of course pure water is not conducting at all. But if we have some buffer solution, small amount of buffer solution added to it, which to make it conducting, we get hydrogen, water split into hydrogen and oxygen and oxygen will be attracted in the anode.

Whereas, hydrogen will be attracted towards hydrogen formation will take place at the cathode. Now standard table gives all the details we need to know about this particular reaction, so once again let me quickly show you delta, this is given here. A for H 2 O liquid it is given here, for H 2 O gas it is slightly different, but we are talking about H 2 O liquid, because the reaction we are talking about is on H 2 O liquid.

For oxygen gas the value is also given here. So, we will use these values, I have put this in order to examine the kinetics in little more details. So, once again the enthalpy and free energy of Gibbs free energy of formation for the elements are 0, whereas for water it is minus 286. I have taken just rounded it to the 0 with decimal place, so we just made it 286. Similarly, delta G is minus 237 and S is equal to 70. Now, delta S once again is product minus reactant.

In this case what are the products? Hydrogen and half mole of oxygen. So, 131 plus 205 by 2 minus 70 joules per Kelvin, which is 163 joules per kelvin. So, T dS given that the reaction is taking place at 298 Kelvin, it is 48.5 kilojoules. So, delta G is now, delta G of reaction is equal to 0 minus of minus 237, that means 237 kelvin, is 237 kilojoules. Now, this is a positive quantity. So, the delta G of reaction, if we just take the individual delta G is, and calculate the delta G of reaction.

We see we need to put in 237 kilos or we need to boost the Gibbs free energy by 237 kilojoules, in order to make this reaction happen. Now, how do we do that? This energy is coming purely from the electrical power, electrical work that we are putting into the system. So, that means we are putting in the current through these two electrodes. So, basically this is the energy is making some electrical work to take place, and this electrical work is creating this additional Gibbs free energy.

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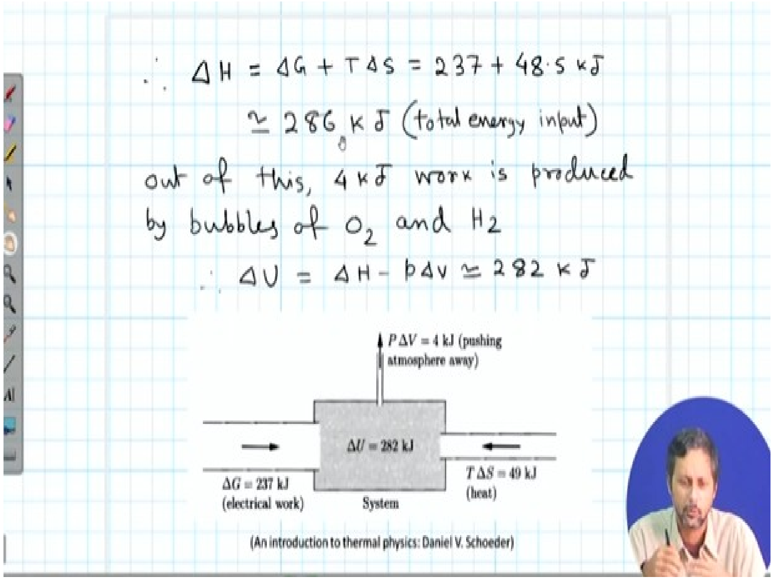

$$\therefore \Delta H = \Delta G + T\Delta S = 237 + 48.5 \text{ kJ}$$

$$\simeq 286 \text{ kJ (total energy input)}$$

out of this, 4 kJ work is produced by bubbles of O_2 and H_2

$$\therefore \Delta U = \Delta H - p\Delta V \simeq 282 \text{ kJ}$$

(An introduction to thermal physics: Daniel V. Schoeder)

Now, if we compute the enthalpy; enthalpy is a combination of and what is this TDS? This TDS is the heat energy that is coming in from the environment. Environment is at 298 Kelvin, the surrounding. So, that surrounding is pumping in these TDS is equal to 48.5 kilojoules of work; 48.5 kilojoules of heat energy into the system. So, all together delta H is equal to delta G plus TDS, which is 286 kilojoules of total energy input needed in order to or for this reaction, for this water splitting to take place.

And out of these 286 kilojoules 4 joules work is produced by bubbles of oxygen and hydrogen and rest 282 kilojoules is stored as internal energy of the system. So, this is just a schematic diagram once again from an introduction to thermal physics by Daniel V. Schoeder, where this process has been described in details. So, we have the system where the total internal energy changes by 282 kilojoules, please remember delta U is equal to delta H minus PDV.

So, that is why we have delta U is equal to 282 PDV of 4 kilo joules, altogether delta H should be 286 kilojoules. Out of that 237 kilojoules is due to electrical work, that is the change in Gibbs energy and 49 kilojoules is due to this TDS, which is heat energy coming in from surrounding. Now, that means if we can make this reverse process to work that means if we can somehow mix hydrogen and oxygen and produce water.

So, basically if we can electrically combine or rather, if we can somehow combine hydrogen and oxygen, then we can make this reverse reaction possible.

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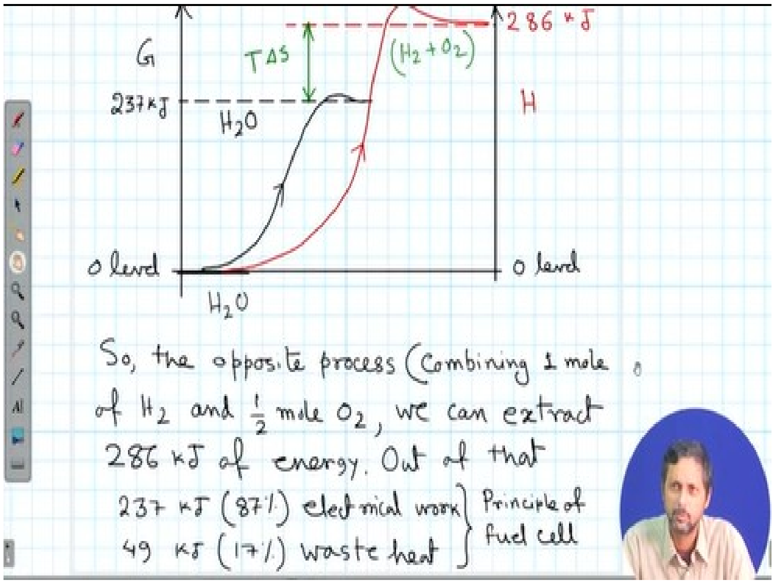

So, the opposite process (Combining 1 mole of H_2 and $\frac{1}{2}$ mole O_2, we can extract 286 kJ of energy. Out of that

237 kJ (87%) electrical work
49 kJ (17%) waste heat
} Principle of fuel cell

Now, if this there is a reverse reaction, so let us first look into this in a diagram, try to understand this in terms of a diagram. Here, we have oxygen + hydrogen, so this is my 0 level of energy. So, this is my Gibbs function, this is my enthalpy function. So, Gibbs energy is changing by 237 kilojoules. So, this is the black line and correspondingly the enthalpy is changing by 286 kilojoules, the difference is TDS.

Of course, I am assuming that there is some small energy barriers, which are due to some non-equilibrium nature of this transformation and all. So, there should be some small hump here, but in significant hump. Now, so that means once this process is complete this H 2 O the water, contains 286 kilojoules of energy in it. Sorry, my mistake; it should be hydrogen and oxygen, so it should be H 2 O here, and hydrogen and oxygen here.

So, this hydrogen and oxygen that contains these 286 kilojoules of enthalpy, out of which we know that only 282 is stored as internal energy. But that is also a good amount of energy. So, if we can somehow reverse this process, so then we can get out 237 kilojoules of electrical work and maybe these 49 kilojoules of heat. Now, 49 kilojoules of heat is only 17%, which will be the waste heat. In the reverse process it will be wasted, but we can get back 87% as electrical work.

And this is the principle of a hydrogen-based fuel cell. Now, fuel cell it was initially thought that it will replace, it will be the source of renewable, the prime source of renewable energy. But of course, although the efficiency is almost 87% as we see here, it has some other technological drawbacks. So, the fuel cell although the research is still going on, we have not got what was promised to us some 30 years back from the fuel cell so far.

But we are still hoping that something good will come out. Now, what we have discussed here is the basic principle of water splitting reaction and the opposite reaction, which is the working principle of a hydrogen fuel cell. So, we will stop here today. This week has been a very fruitful week, where we have learned about concepts like free energy. We have concern we have understood the concept of thermodynamic equilibrium and what are the roles of free energy in achieving those equilibrium.

And next we are going to take up a very important phase or very important field of thermodynamics, which is phase transition. This is once again the process which takes place at constant pressure and constant temperature. So, let us wait till next week, to learn about phase transition and goodbye for now.