Course: Adsorption Science and Technology: Fundamentals and Applications

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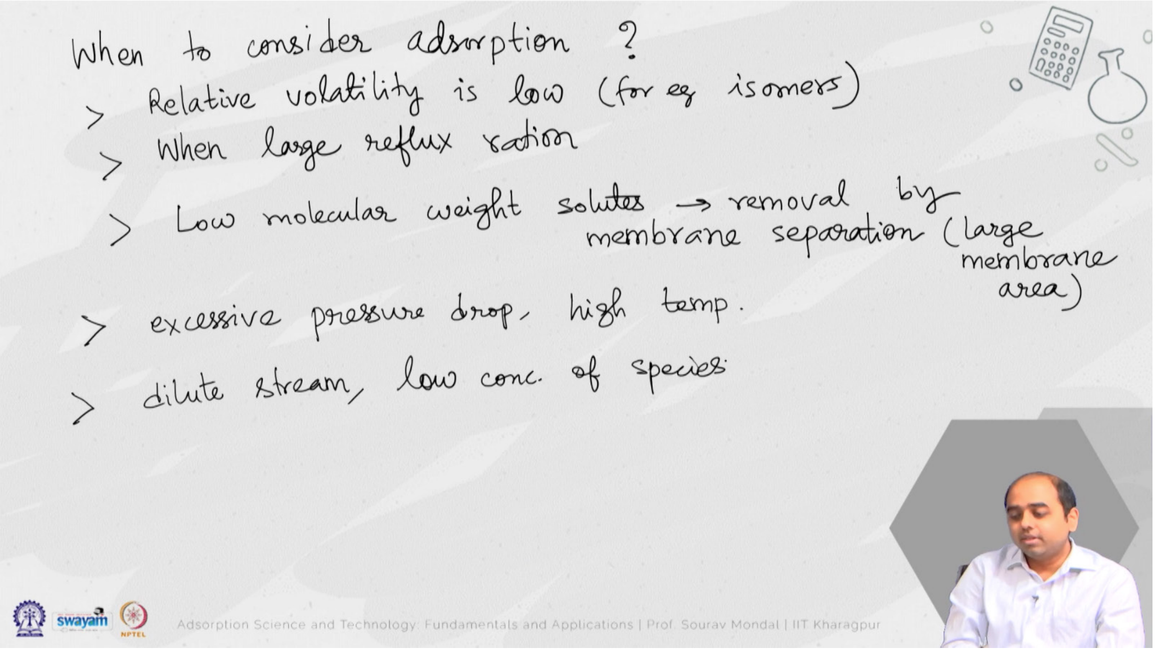
Week 01

Lecture 3 | Key Features of Adsorption, Thermodynamic Background

Hello everyone, welcome to this third lecture on this course of adsorption. So, in the previous two lectures you have seen that we discussed about the background of this adsorption and the last class we talked about the types of adsorbents and its key feature. So, in this class we will talk about the process of adsorption in more detail and particularly from a thermodynamic perspective. So, as you know adsorption is a equilibrium based process and that is why thermodynamics of this process is very important. Particularly in this system, where the equilibrium plays a big role and there is an associated change in the free energy of the system being a spontaneous process. It is pertinent that we should talk about the thermodynamics of the system.

So, to start with when essentially do we consider adsorption? So, typically you know other separation based processes, for example, distillation, membrane separation, absorption AB, liquid extractions are also possible alternatives. But in the context of having high efficiency or high selectivity, adsorption is the most preferred choice. So, as a process engineer or as a system engineer, it is important for you to decide when you want to consider or when you should consider adsorption as a possible option for your downstream processing. So, when to consider adsorption? is a question that we should make appropriate decision at the process level itself.



When to consider adsorption ?

- > Relative volatility is low (for eg isomers)
- > When large reflux ration
- > Low molecular weight solutes → removal by membrane separation (large membrane area)
- > excessive pressure drop, high temp.
- > dilute stream, low conc. of species

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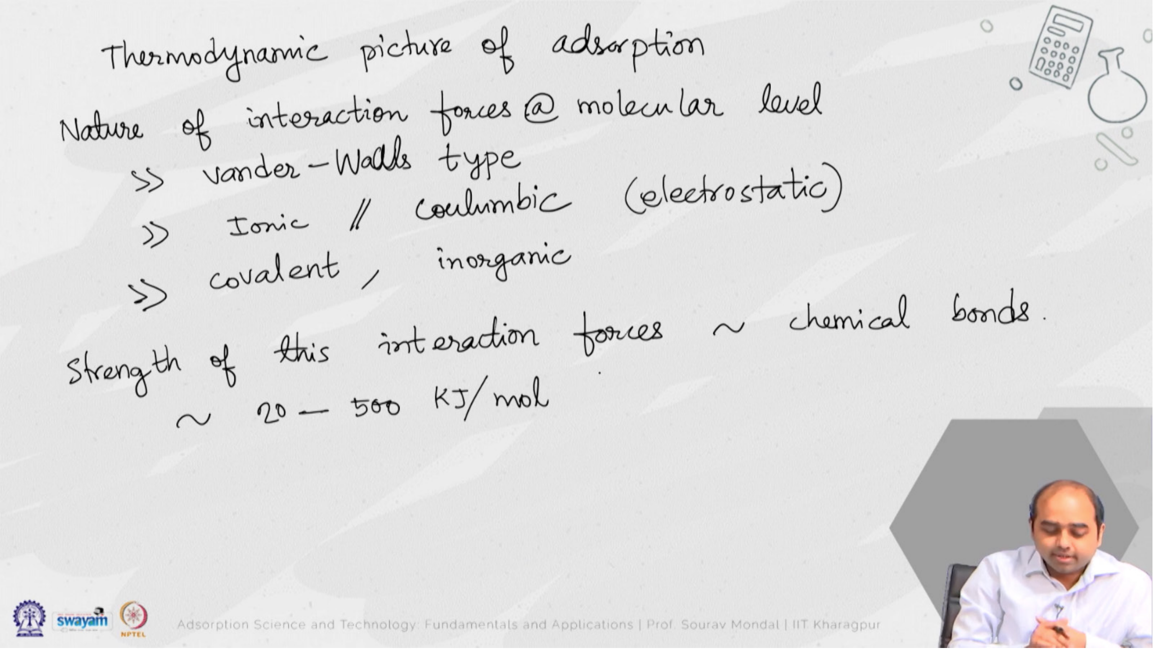
So, if the relative volatility of the molecule is low, distillation may not be an economic choice, right. For example, isomers, stereo isomers distillation is of course, not a preferred choice in that case. When you need large reflux ratio for close boiling compounds, formation of azeotropes. These are some of the situations where distillation is of course, not a preferable choice. Low molecular weight solutes if they are to be removed, by membrane separation, you would generally need a dense membrane for which permeability is very low or the throughput is very low.

So, large membrane area would be needed and this is economically not a good choice. Excessive pressure drop or high temperature operation is energetically not a viable option and one would like to go for alternative options and adsorption is one of the preferred choice. Dilute stream or low concentration of species is something which may be very difficult to remove or may not be cost effective in other processes and this is where you know adsorption based process are generally very useful or very economically feasible option that one should consider. Of course, there are some situations where you cannot have adsorbent processes is particularly when regeneration of the adsorbent itself, is very difficult and it is again economically not very feasible to use your system with fresh adsorbents every time. This is one situation when adsorption cannot be used.

If the capacity of your adsorbent towards the target species is very low or the time needed to reach the equilibrium is also very low, is something I mean these two are more or less interlinked you will soon realize. Then adsorption is of course, not a very good choice because you would need a large quantity of your adsorbent and of course, that involves other process constraints. Next let us talk about the background from a thermodynamic perspective. This adsorption process is generally facilitated by intermolecular interactions. So, which are mostly.



Thermodynamic picture of adsorption

Nature of interaction forces @ molecular level

>> vander-Walls type

>> Ionic // coulumbic (electrostatic)

>> covalent, inorganic

Strength of this interaction forces ~ chemical bonds.

~ 20 — 500 KJ/mol

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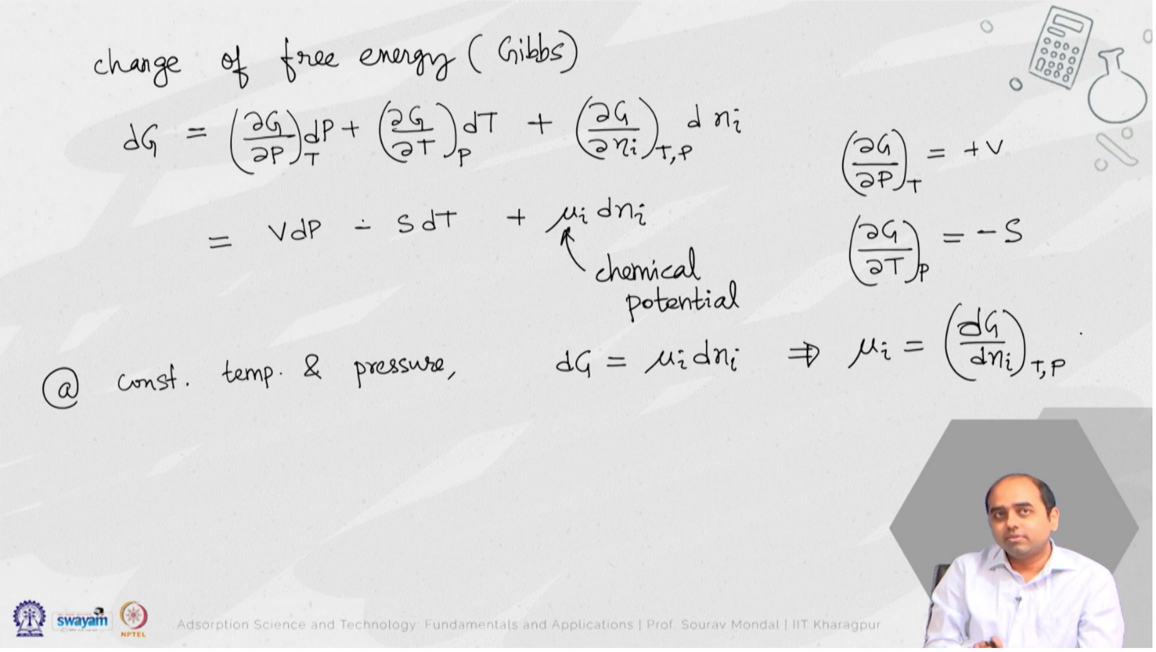
So, which is mostly the nature of these interaction forces at the molecular level, could be of Van der Waals type nature. It could be ionic in nature, ionic or coulombic in nature or electrostatic essentially. It could be covalent bonding, inorganic bonding. Typically, the strength of this interaction forces is comparable to the chemical bonds, and it could range somewhere between 20 to almost 500 kilojoule per mole. So, this is the kind of the free energy change that we are you know talking about based on this interactive or this interaction forces.

Now, coming to the thermodynamics, we know that the change in the free energy or essentially change in the Gibbs free energy, can be represented by the Maxwell relations, where each of these partial derivatives can be represented from the Bonn expressions in Maxwell relations and they can be represented as in this format. I hope the process symbols all are self-explanatory just to make sure that we are, you know, not confused with the Maxwell relations. I am also writing them down. So, s is the entropy and mu_i is the chemical potential, n is the moles species that we are talking about. Now of course, change in the Gibbs free energy with respect to the moles or the mole number is essentially the chemical potential.

So, that is what is represented by this chemical potential is not it. So, at constant temperature and pressure, change in free energy can be represented in this form or the chemical potential can be represented in terms of the change in the free energy. Now in terms of the free energy change. So, this is what we represent the change in the or the chemical potential of the system depending on the change in the free energy. So, if the since the free this chemical potential is reduced at the attachment size, the change in the free energy is negative because as you know all mass transfer processes happens or occurs due to a chemical potential gradient.



change of free energy (Gibbs)

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i$$

$$= VdP - SdT + \mu_i dn_i$$

μ_i ← chemical potential

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

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

@ const. temp. & pressure, $dG = \mu_i dn_i \Rightarrow \mu_i = \left(\frac{dG}{dn_i}\right)_{T,P}$

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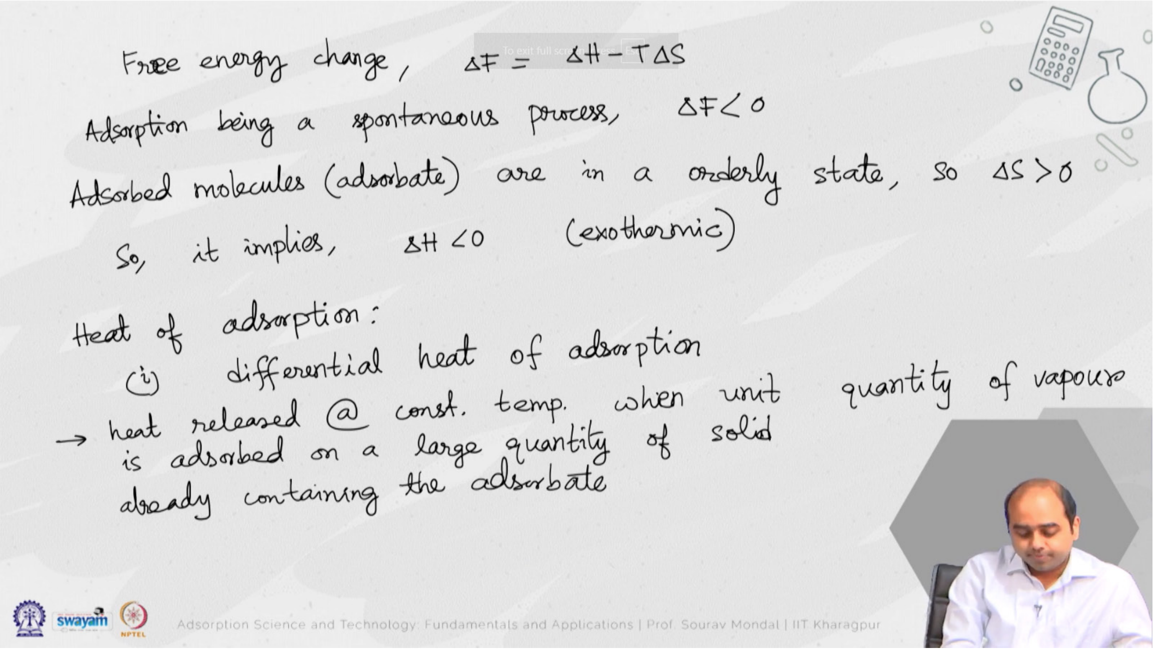
So, in this case being a spontaneous process, the free energy change being negative, the system moves towards a lower chemical potential state. Now I will also try to describe the free energy change in terms of the enthalpy and the entropy of the system. So typically we can write the free energy change delta F as delta H minus T delta S, this something all of you have already aware of. Adsorption being a spontaneous process delta F change is negative and the adsorbed molecules known as the adsorbate are in a orderly state. So, the change in the entropy is positive.



Free energy change, $\Delta F = \Delta H - T\Delta S$

Adsorption being a spontaneous process, $\Delta F < 0$

Adsorbed molecules (adsorbate) are in a orderly state, so $\Delta S > 0$

So, it implies, $\Delta H < 0$ (exothermic)

Heat of adsorption:

(i) differential heat of adsorption

→ heat released @ const. temp. when unit quantity of vapours is adsorbed on a large quantity of solid already containing the adsorbate

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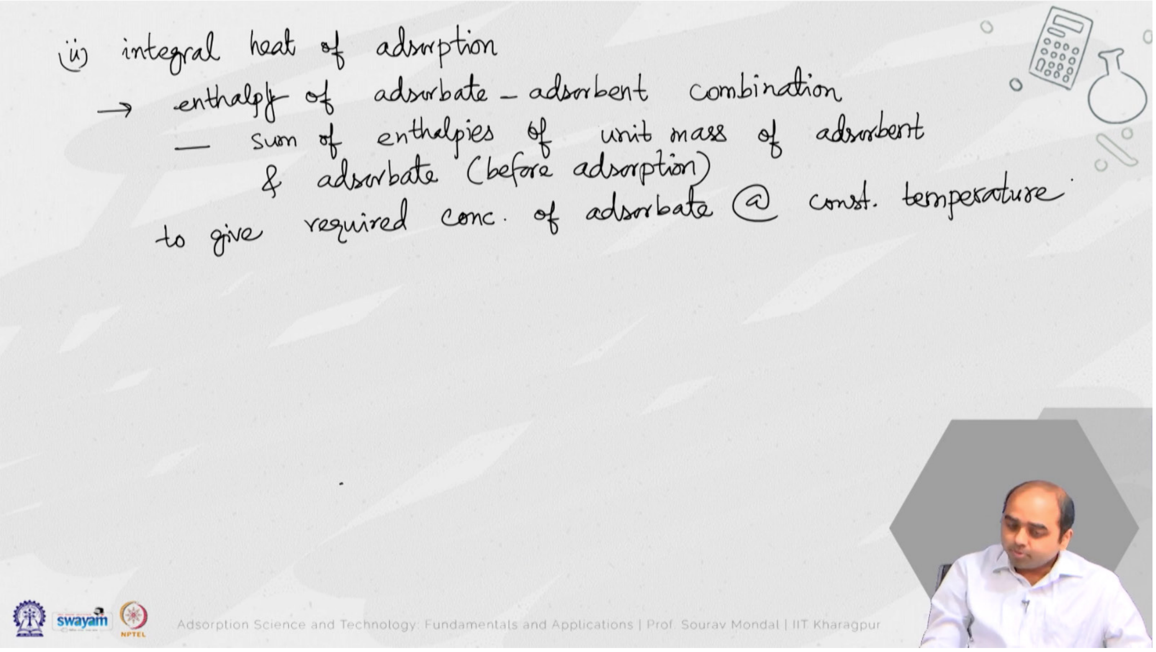
So, it implies that delta H is less for a adsorption process which means there is release theoretically, a release of energy during this adsorption process. Typically, the release of energy is very low to be practically measured and this is what referred to as the heat of adsorption. So, there are two types of heat of adsorption, one is the differential heat of adsorption. So, the differential heat of adsorption is defined as the heat liberated at constant temperature. Heat released at constant temperature when unit quantity of vapor or gas is as adsorbed on a large quantity of solid, already containing the adsorbate.

Generally the adsorbate concentration is unchanged. So, this is referred to as the differential heat of adsorption. There is another heat known as this integral heat of adsorption. So, it is the enthalpy of this you know defined in this way, enthalpy of adsorbate-adsorbent combination subtracted by the sum of enthalpies of unit mass of adsorbent and adsorbate, of course before adsorption to produce the required concentration of adsorbate at constant temperature. So, this two heats of adsorption, the differential heat of adsorption or the integral heat of the adsorption, both of them relates to the amount of the heat or the energy change involved in this adsorption process.



(ii) integral heat of adsorption

→ enthalpy of adsorbate – adsorbent combination

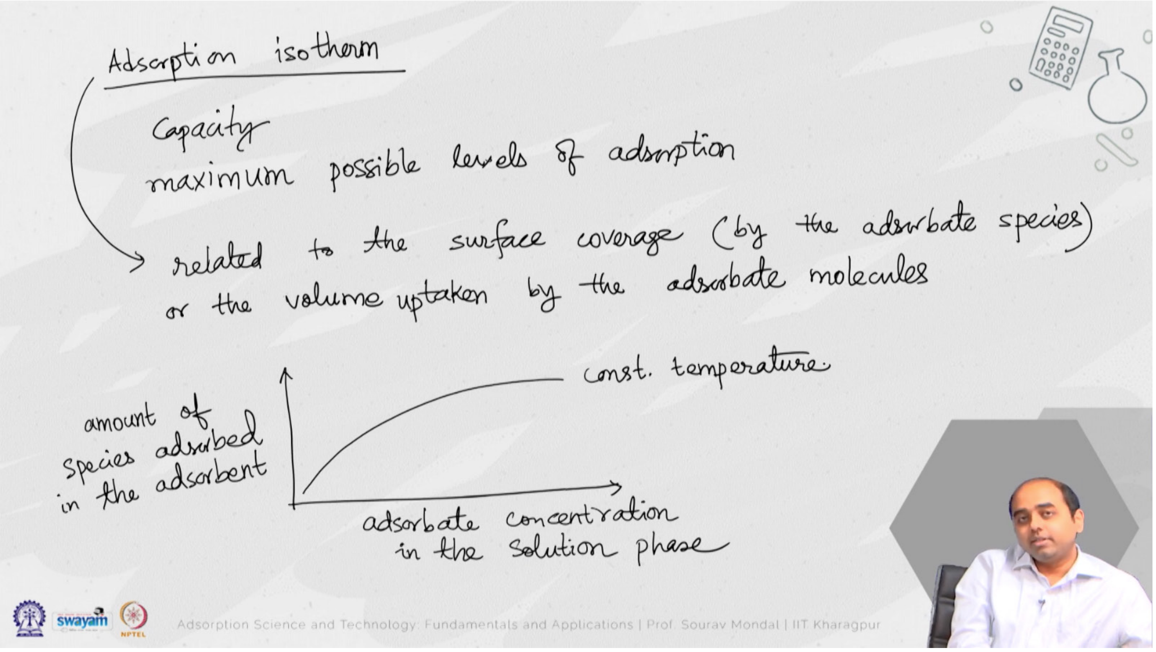
— sum of enthalpies of unit mass of adsorbent

& adsorbate (before adsorption)

to give required conc. of adsorbate @ const. temperature

They also gives you an extent or an idea on the extent of the interactive forces which is prevalent in this process. Now, specifically both these heat of adsorption are measured at constant temperature ah which brings us to the idea of this adsorption isotherm. So, this adsorption isotherm is essentially a correlation between the amount of adsorption which happens or the uptake of the desired or target species which happens as a function of its concentration in the bulk phase at constant temperature. So, this gives you an idea of the capacity of the adsorption. The maximum possible levels of absorption by this adsorbent.

So, this adsorption isotherm gives you know direct or a quick overview on the amount of the adsorption which is possible in a particular you know environment at a constant temperature for a particular adsorbent. So, this is related. So, this adsorption isotherm is directly related to the you know the surface coverage, of course, by the adsorbate species or the volume taken up or up taken by the adsorbate. So, typically this is a plot of the amount of species adsorbed as a function of the adsorbate concentration in the solution phase. And this is generally evaluated or estimated at constant temperature.



Adsorption isotherm

Capacity

maximum possible levels of adsorption

related to the surface coverage (by the adsorbate species) or the volume uptaken by the adsorbate molecules

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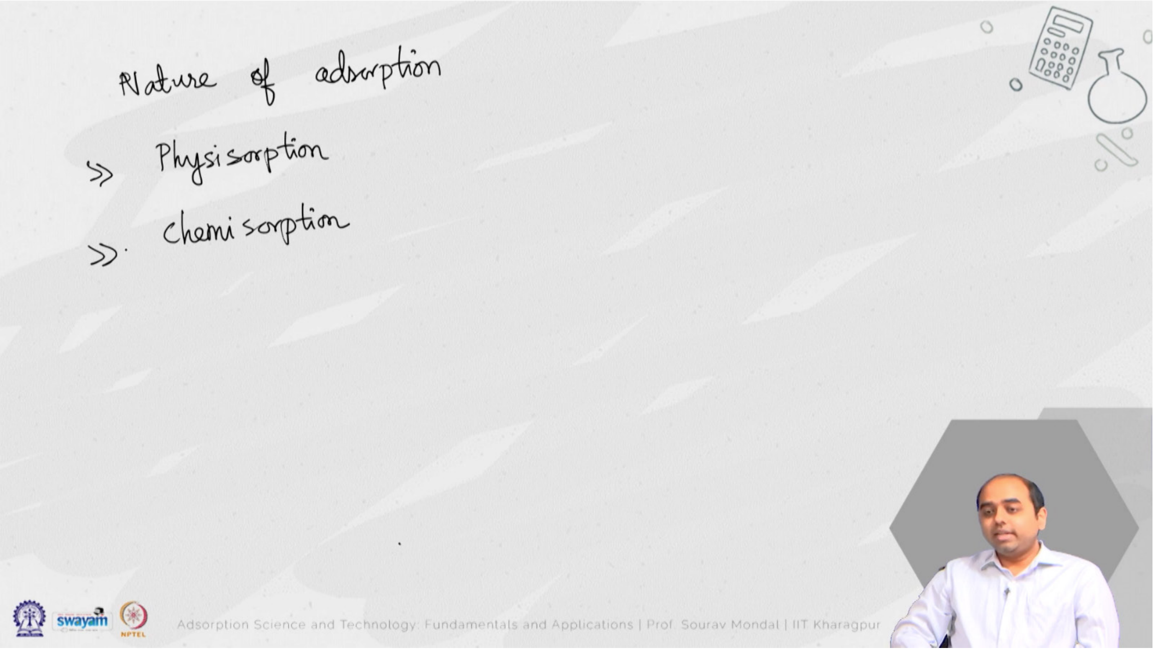
So, this is the thermodynamic background behind this adsorption process and this gives us very useful information about the particularly the capacity as well as the level of adsorption which is possible, in a particular temperature. Now typically the adsorption isotherm relates a constant temperature process and these heats of adsorption gives you an idea about the level of intermolecular interactions that is present in this process. In this context I would also like to describe two other things. One is the nature of adsorption whether it is physisorption or whether it is chemisorption. So, I like to emphasize that both physisorption or chemisorption are adsorption processes.

Chemisorption is not to be confused with chemical reaction. The difference between these two stands in the level of the free energy change of the process. So, typically in chemisorption the free energy change is much much higher compared to a physisorption process and that is the reason when you have chemisorption or when you have, you know, very high a energy change associated during adsorption process and that is what chemisorption is. The regeneration of the adsorbent becomes very difficult because the strength of the you know this binding is significantly higher compared to the other case. So, physisorption based process are easy to regenerate chemisorption are not so easy to regenerate.



Nature of adsorption

- Physisorption
- Chemisorption

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So, chemisorption involves where the free energy change is higher as well as the associated heat evolution or the energy change during this process is also higher. And, energetically this is much more a stable formation of the adsorbent-adsorbate combination compared to a physisorption process. The magnitudes of this energy varies with different adsorbents and typically chemisorption is at least the energy change in that process is at least 5 to 20 times higher compared to a physisorption level. So, with this I would like to close this lecture in this topic.

Hope you find it useful. Thank you.