Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 08

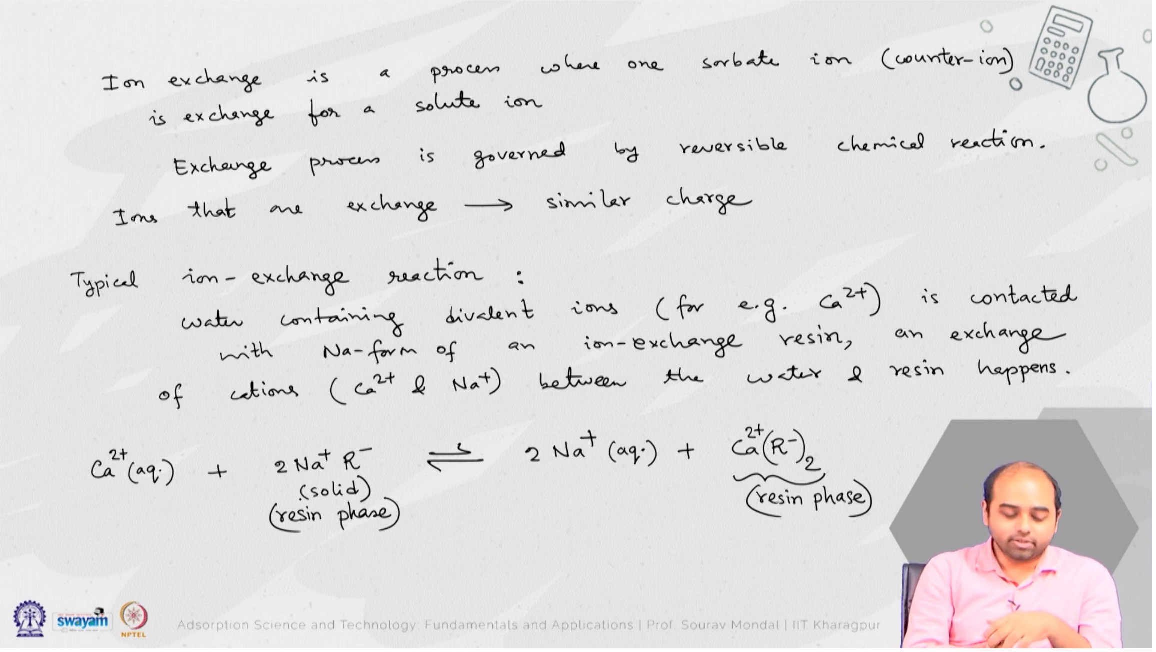
Lecture 36 | Ion Exchange: Principles

Hello everyone, welcome to this last week of this course on adsorption science. In this week we are going to talk about ion exchange and how the ion exchange is related to this world of adsorption science and technology. So, basically ion exchange is a process in which the ion between the solution phase and the solid phase is exchanged. Now this is not an adsorption process in principle I would say rather this is an this exchange is more like a reversible stoichiometric equivalent chemical reaction. So this ion exchange, this ion exchange is a process of or is a process where one sorbate ion which is generally referred to as the counter ion in this case is exchanged for a solute ion. And this exchange process is governed by reversible chemical reaction.

So, in the true sense this is a reversible chemical reaction of the ions, but since the exchange is between a solid and a liquid phase or the solution phase and this involves this you know equilibrium established between this exchange process in this reversible phenomena. This is analogous to adsorption signs and these separation process can be equated to very similar to the adsorption equilibrium process how and that is something we are going to be discussing throughout this week and its background the solid sorry the ions that are exchanged ions that are of that are exchanged is of similar charge as you can realize you cannot replace a positive ion with a negative ion. So, in general in general it is the cation which is replaced from the solution because this ion exchange process is classically used for you know softening water or in water treatment systems particularly where you want to reduce the chemical hardness of the solution or you want to purify the solution and improve its TDS or mineral content. So, mostly it is the positive ion or the cations which are exchanged in this process.

So, for example, if you have you know ion exchange column which are generally or mostly resin in nature and something what about this as adsorbents here we will talk about in the next lecture, but typically an ion exchange reaction. Let us say if you are contacting your calcium ions. So let us say you have water containing divalent ions for example calcium is contacted with sodium form of an ion exchange resin. So, then an exchange of cations that is calcium and sodium between the water and resin happens. So, in this case, the sodium ion is the counter ion and calcium is the solute ion present in the solution phase.

So, the chemical reaction this process ion exchange process can be represented by chemical reaction. So, we can write this as this is in aqueous phase, plus. So, R represents the solid. So, this is like the solid or the adsorbent phase reversible chemical reaction. So, now sodium ion comes in the aqueous phase and resin comes in the sorry the calcium comes in the resin phase.



Ion exchange is a process where one sorbate ion (counter-ion) is exchange for a solute ion

Exchange process is governed by reversible chemical reaction.

Ions that are exchange → similar charge

Typical ion-exchange reaction:

water containing divalent ions (for e.g. Ca^{2+}) is contacted with Na-form of an ion-exchange resin, an exchange of cations (Ca^{2+} & Na^{+}) between the water & resin happens.

$$Ca^{2+}(aq.) + \underset{\substack{\text{(solid)}\\ \text{(resin phase)}}}{2\,Na^{+}R^{-}} \rightleftharpoons 2\,Na^{+}(aq.) + \underbrace{Ca^{2+}(R^{-})_2}_{\text{(resin phase)}}$$

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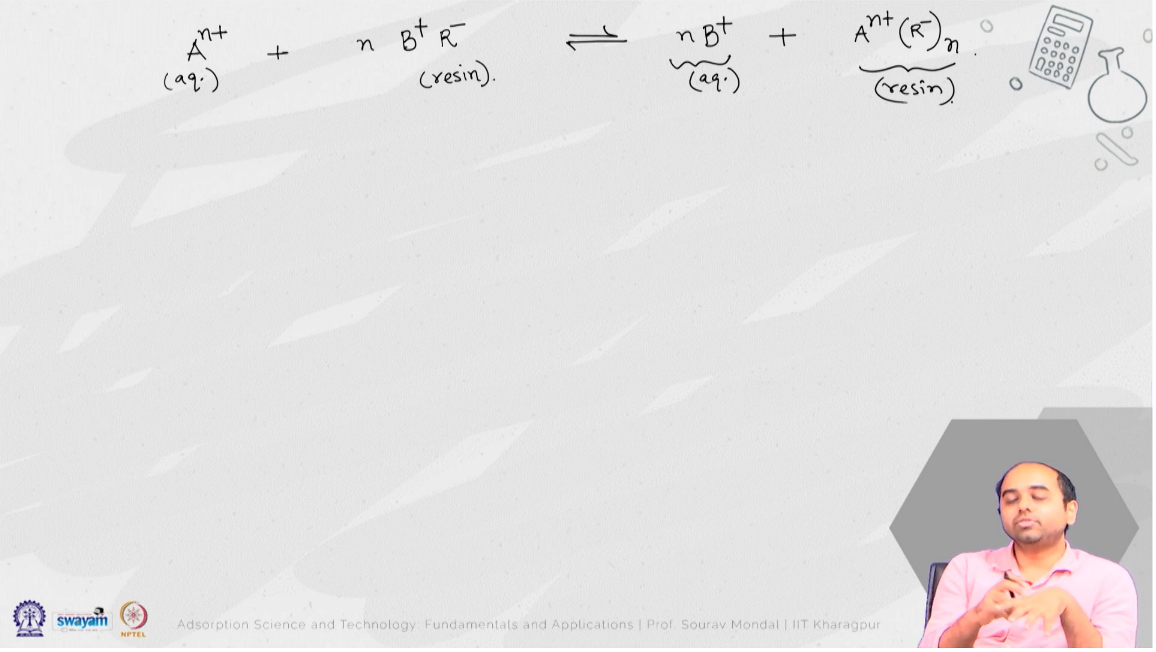
So this is like a resin phase which is solid in nature. So this is how a reversible you know chemical reaction can be written down. We will talk about the resin structure and its molecular details and everything in the next class. But in this class today we are going to talk about this how this chemical reaction here can be represented by the law of mass action or how we can quantify the you know these exchange capacities are analogous to the equilibrium adsorption capacity between these two you know between this exchange process. So, we can write for a generic system.

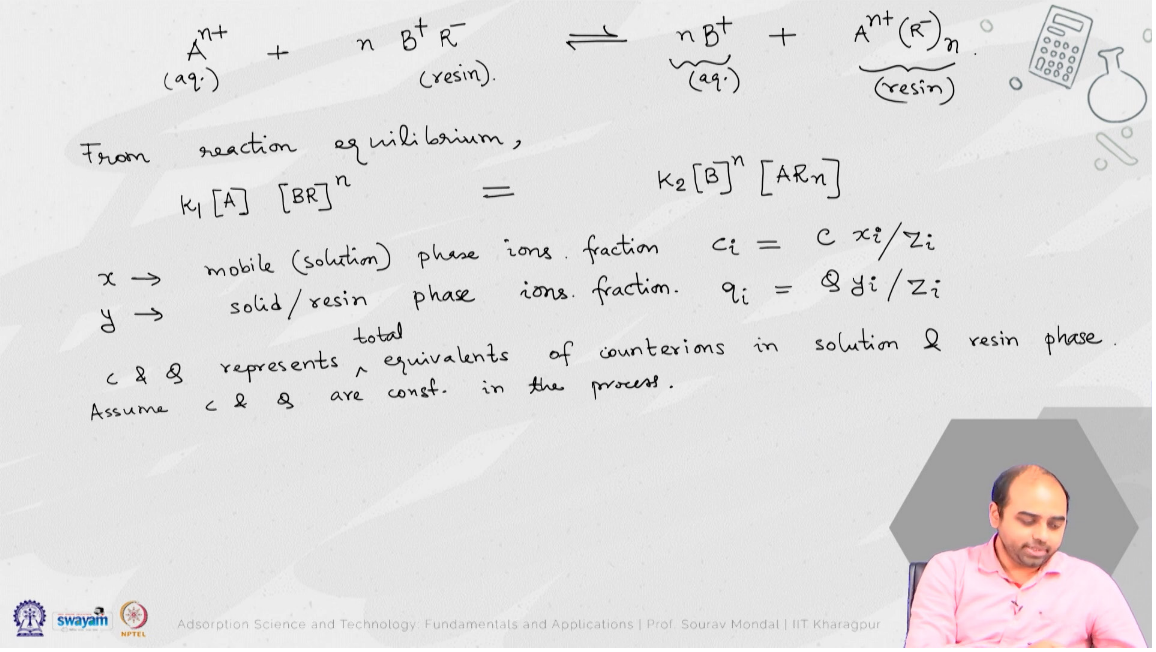
So, let us try to write down a generic reversible chemical reaction. In this case we are trying to write down for a generic n valent system. So, this is the aqueous phase ion. This is the resin phase ion. Sorry, it is B plus R minus.

This can be written down as n B plus plus A n plus R minus n. So, this is again in the aqueous phase and this is again in the resin phase. So, what we notice through this ion exchange process is that the ions solute ions present in the the solution goes into the resin phase or get bounds to the resin phase and it is a in in that process you are able to remove these ions from your solution by this you know ion exchange resin. And, in the process you are introducing new counter ions from the resin to your solution. Now, if those new ions is something that you want them to be you know favourable.



$$\underset{(aq.)}{A^{n+}} + n\,\underset{(resin).}{B^{+}R^{-}} \rightleftharpoons \underbrace{n\,B^{+}}_{(aq.)} + \underbrace{A^{n+}(R^{-})_n}_{(resin)}.$$

So, for example, if you are able to replace your calcium ions with sodium ions, then you are able to reduce your hardness, fouling, corrosion behaviour significantly in your solution. And that is the whole idea behind this treatment of ion exchange that you are not essentially removing this you know ion completely as in a adsorption situation you are able to remove certain you know contaminants from water. Here you are replacing the undesired ions with some desirable or favorable ions from this system which improves the water quality and in this process you are able to remove the ions that is of undesirable nature particularly this calcium magnesium you know compounds or something else some ionic compounds that can be removed from the system by this chemical reaction. So, this is even though this is a chemical reaction this still has the flavor of this adsorption behavior from this equilibrium theory as well as the presence of a solid phase trying to remove or capture ions from the liquid phase is something also very similar to the way how adsorption works where you try to remove you know solutes from your solution phase into the solid phase, but in this case you are doing this exchange process or a replacement scenario. So, now from the reaction equilibrium how we can write down this rate of forward and backward process.



$$\underset{(aq.)}{A^{n+}} + n\,\underset{(resin).}{B^+R^-} \rightleftharpoons \underbrace{nB^+}_{(aq.)} + \underbrace{A^{n+}(R^-)_n}_{(resin)}.$$

From reaction equilibrium,

$$k_1[A]\,[BR]^n = k_2[B]^n\,[AR_n]$$

$x \rightarrow$ mobile (solution) phase ions. fraction $c_i = c\,x_i/z_i$

$y \rightarrow$ solid / resin phase ions. fraction. $q_i = Q\,y_i/z_i$

c & Q represents total equivalents of counterions in solution & resin phase.

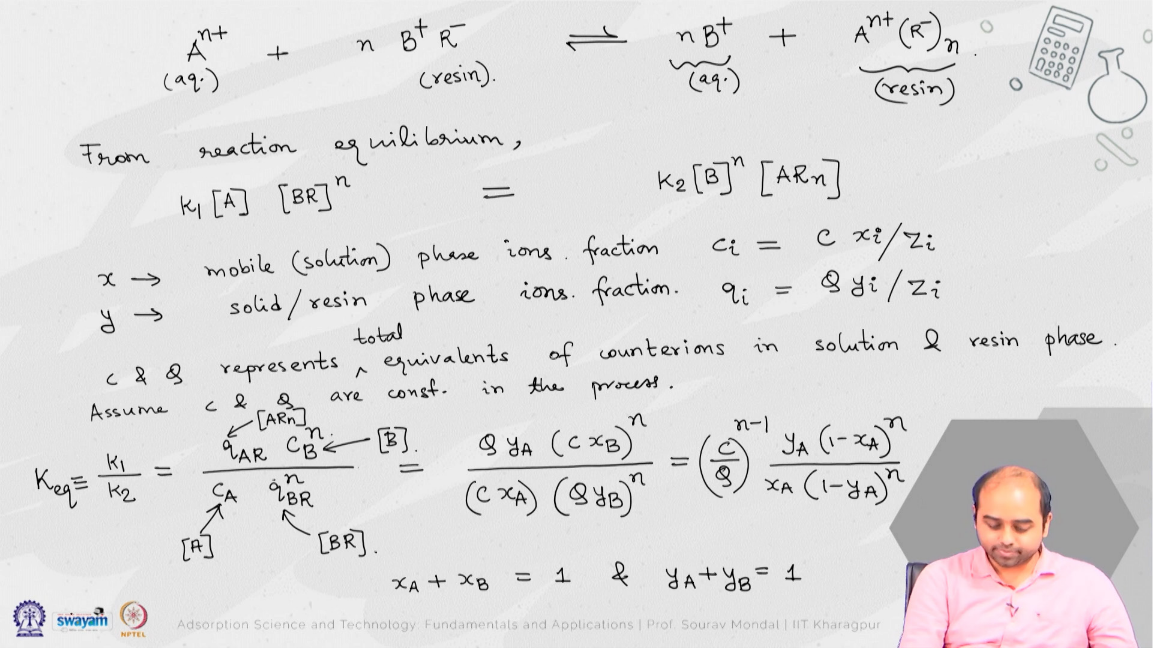
Assume c & Q are const. in the process.

So, the rate of forward process is we are assuming all of these exchange processes first order in sorry depends on the coefficient it could be first order or the nth order. So, A and for the case of the solid phase this is n. So, this is like the forward reaction and the backward reaction would be k 2 B to the power n and here we have A R n right. So, the coefficient comes in the power based on the molecularity of this reaction and this is equal at equilibrium. So, the rates of forward and the backward process is equal.

Now let us try to define the you know the ions in the solid phase or the ionic fraction or the mole fraction of the ions in the solid phase and in the solution phase separately. So what we mean is this we write x as the mobile phase or solution phase you know ions y as the solid phase solid or resin phase ions. right we are writing down the. So, this is like the you know ionic concentration now we are writing down the concentration of the particular species in this case let us call it as C i which is like the solution phase as like the total concentration C multiplied with the mole fraction divided by the valence of that ion zi. And similarly for the case of the solid phase we can write I am using the notation analogous to the adsorption scenario where we write the scenario for q or the this concentration in the solid phase as capital Q yi by zi.

So, here capital C and capital Q represents the equivalence of counter ions in solution and resin phase right. And it is also assumed that also assumed that this C and Q total concentrations miss the word total are constant in the process. So, having said this what we can do is write down these equilibrium relation in terms of you know capital C and capital Q and then we can see how we can write down that in terms of x and y already is that the equivalent, you know this fractions of this. So, these are like mobile phase ion fraction I would write y is the solid phase ion fraction. So, how these ionic fractions can be related.

So, this holds both for A and for B. Now coming to this you know this constant or if you rearrange this equation A and B what it turns out is this we can write down k 1 by k 2 is something like qAR multiplied with C B to the power n, right where I am writing down in terms of this C of B and then C of you know q of AR to designate that this is in solid phase and this is in you know solution phase. So, this represents A R n this represents the B and in the denominator we have C B and q B R to the power n so this sorry C A concentration of A and this represents concentration of B R. Since R phase or resin phase is in solid we write that concentration in terms of q or the solid concentration and A and B is in solution phase, we write that in terms of C. So, this is how we are writing down the concentrations for this case.



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Assume c & Q are const. in the process.

$$K_{eq} \equiv \frac{k_1}{k_2} = \frac{\overset{[ARn]}{q_{AR}}\;\overset{[B].}{C_B^n}}{\underset{[A]}{C_A}\;\underset{[BR].}{q_{BR}^n}} = \frac{Q\,y_A\,(c\,x_B)^n}{(c\,x_A)\,(Q\,y_B)^n} = \left(\frac{c}{Q}\right)^{n-1}\frac{y_A\,(1-x_A)^n}{x_A\,(1-y_A)^n}$$

$$x_A + x_B = 1 \quad \& \quad y_A + y_B = 1$$

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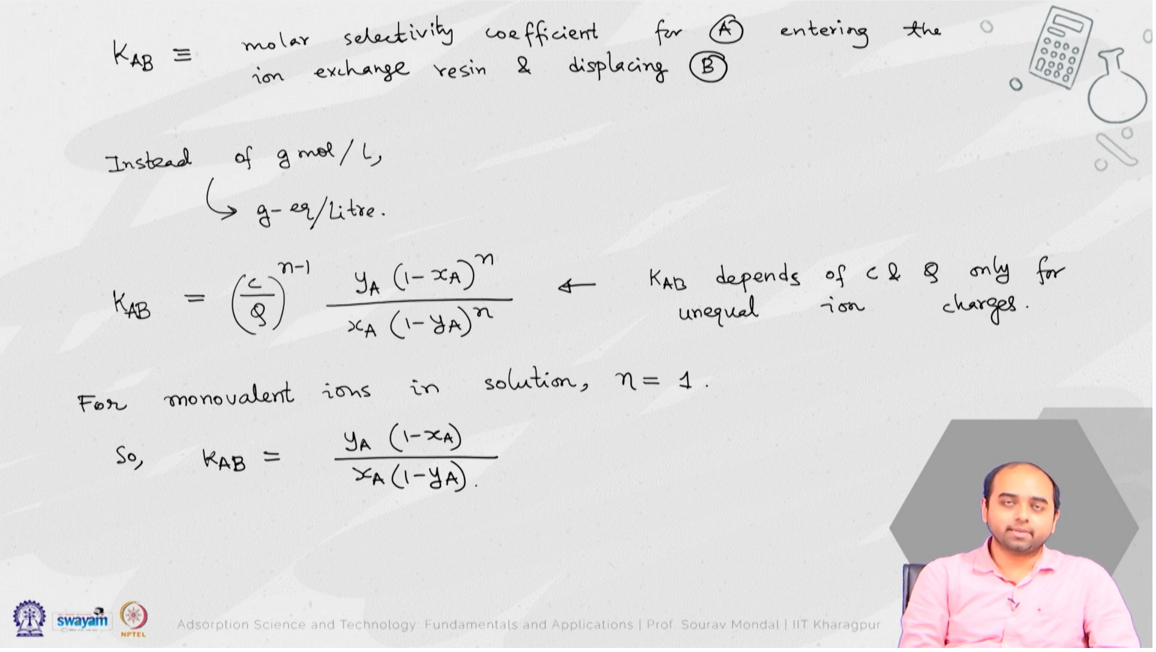
Now, substituting you know qBR and you know CA qAR from these two relations, one can write this to be Q into yA, zi would cancel out all right Q into yA times C into xB right capital C into xB to the power n divided by CA can be written down as capital C into xA times q into yB to the power n. right. Now since you know this xA plus xB is equal to 1 and yA plus yB is also equal to 1. So, that electrically the solution phase and the resin phase the total charge is conserved. So, naturally the mole fractions of the ions of both type A and B types in the solution phase and in the resin phase would be equal to 1 the summation should be equal to 1.

So with this you know information one can write down for the case of only for the case of the component A which is present in the solution as this theory. We just substitute this you are going to get this relation . So, this is the relation for this capital K equivalent in this case or the this equilibrium constant which can be related to the similar type of equilibrium constant that we have seen in adsorption process. But please note that this this coefficient or this constant that we get here this capital K A comma B, this is essentially more of a molar you know selectivity coefficient or this a entering the ion exchange resin and displacing solute B. So, for the for the you know this resin phase and versus for the you know this solution phase both the concentrations are actually written down in terms of its you know this milli-equivalents and that is a very important concept that we write down this information in gram milli-equivalent maybe I should highlight this what we mean by gram milli-equivalent that instead of writing instead of writing this gram moles per liter, what is written down is something known as gram equivalent per liter.

So, this essentially means that ions present in the solutions could have different you know charges thus it is important to that is why it is important to you know mention this that the total concentration of the ions in terms of its gram equivalent and not as gram moles. So, that is how why this gram equivalent or the equivalent is more you know popular or used to convention in this you know this topic of ion exchange. Now, coming back to this this equilibrium constant K AB in this case which we got, it is important to realize that in replacing. So, n here stands for the valency in replacing this or you know further using this relation. So, for monovalent ions in solution right.



K_{AB} ≡ molar selectivity coefficient for Ⓐ entering the ion exchange resin & displacing Ⓑ

Instead of g mol/L,
↳ g-eq/Litre.

$$K_{AB} = \left(\frac{C}{Q}\right)^{n-1} \frac{y_A (1-x_A)^n}{x_A (1-y_A)^n}$$ ← K_{AB} depends of C & Q only for unequal ion charges.

For monovalent ions in solution, $n = 1$.

So, $$K_{AB} = \frac{y_A (1-x_A)}{x_A (1-y_A)}.$$

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Generally, the ions that are present in the resin are monovalent in nature. So, the monovalent ions which is present in the solution in that case this n is equal to 1. K AB is independent. So, this becomes yA into 1 minus xA . So, interestingly it becomes.

So, for monovalent ion exchange process the equilibrium constant is independent of the total amount or the total concentration of the you know ions present in the solution phase as well as in the resin phase. So, in the case of I will repeat this once again in the case of monovalent ion exchange process this ionic constant or this equilibrium constant or whatever this capacity of the ion exchange process is actually independent of the total mass or not total mass total amount or the total concentrations of these ions or equivalent concentration of these ions present in the solution phase and in the resin phase that is not important that does not play a role in determining the equilibrium capacity in this case. So, this this is only important. So, this suggest this the this K AB depends on C and Q only for unequal counter ion charges or I would say simply ion charges. Both in the solute and in the resin phase.

So, in the case of monovalent or when n is equal to 1 then this is independent of the total concentration of these ions present in the solutions. So, this is a very important you know this relation both for unequal charges and equal or monovalent charges and in this case this total concentration is becomes important for unequal distribution of these charges both in the solution and the resin phase. So, with this I would like to close this lecture. In the next class, we are going to talk about the different types of resin what are the typical you know equilibrium constant values for those scenarios. Thank you I hope all of you found this lecture useful.

I believe you found some connection between the reversible chemical reaction which is applicable in this case to the process of adsorption. Thank you.