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# Thermodynamics of Ion Exchange

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## 1. Introduction

### 1.1. Ion exchange equilibria

During an ion exchange process, ions are essentially stepped from the solvent phase to the solid surface. As the binding of an ion takes place at the solid surface, the rotational and translational freedom of the solute are reduced. Therefore, the entropy change ( $\Delta S$ ) during ion exchange is negative. For ion exchange to be convenient, Gibbs free energy change ( $\Delta G$ ) must be negative, which in turn requires the enthalpy change to be negative because  $\Delta G = \Delta H - T\Delta S$ . Both enthalpic ( $\Delta H^\circ$ ) and entropic ( $\Delta S^\circ$ ) changes help decide the overall selectivity of the ion-exchange process [Marcus Y., SenGupta A. K. 2004]. Thermodynamics have great efficiency on the impulsion of ion exchange. It also sets the equilibrium distribution of ions between the solution and the solid. A discussion about the role of thermodynamics relevant to both of these phenomena was done by researchers [Araujo R., 2004].

As the basic rule of ion exchange, one type of a free mobile ion of a solution become fixed on the solid surface by releasing a different kind of an ion from the solid surface. It is a reversible process which means that there is no permanent change on the solid surface by the process. Ion exchange has many applications in different fields like enviromental, medical, technological,.. etc. To evaluate the properties and efficiency of the ion exchange one must determine the equilibrium conditions. At equilibrium conditions no mass diffusion and concentration gradients occur through the surface of ion exchanger. Ion Exchange equilibria can be explained by plotting the concentration( $C_A^{s+}$ ) or equivalent fraction( $x_A^{s+}$ ) of  $A^+$  at the surface versus the concentration ( $C_A^+$ ) or equivalent fraction( $x_A^+$ ) of this ion in the equilibrium solution. For monovalent ions the equivalent fractions are given by [1];

$$x_A^{s+} = \frac{m_A^{s+}}{m_A^{s+} + m_B^{s+}}$$

$$x_B^{s+} = \frac{m_B^{s+}}{m_A^{s+} + m_B^{s+}} \quad (1)$$

Where  $m$  denotes the concentration of the specified ions at the surface. Ion exchange reactions may be described by the law of mass action using the activities of the ions, rather than their concentrations [Bergaya et al., 2006];

$$K = \frac{a_B^{s+} a_A^+}{a_A^{s+} a_B^+} \quad (2)$$

where  $a_A^+$  and  $a_B^+$  are the activities of ions  $A^+$  or  $B^+$  in solution  $a_A^{s+}$  and  $a_B^{s+}$  the activities of these ions at the surface of the exchanger.  $K$  represents the thermodynamic equilibrium constant. To explain ion exchange equilibria some common models are used. First type of this model is based on the mass action law [Gorka et al., 2008; de Lucas et al., 1992; Melis et al., 1995; Valverde et al., 1999]. In the second group ion exchange is treated as an adsorption process [Gorka et al., 2008] and in the third, the solid phase is considered to provide sites with fixed charges for ion exchange, as well as sites on which molecular adsorption takes place [Gorka et al., 2008; Novosad & Myers, 1982; Myers & Byington, 1986; Ioannidis & Anderko, 2001].

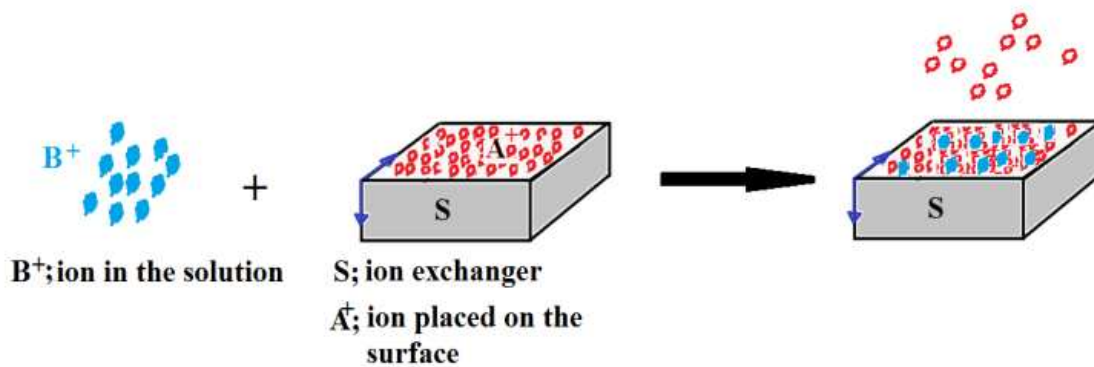
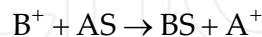


Figure 1.



## 1.2. Ion exchange isotherm

The ion exchange equilibrium can be qualified by suitable equilibrium isotherms. These isotherms are a graphical representation of the correlation between the equilibrium and experimental terms at constant temperature. The concentration of an ion in the solid expressed as a function of its concentration in the solution under specified conditions and at constant temperature. The most common ion exchange isotherm represents solidarity between ionic compositions of two phases: the ion exchange material and solution [Zagorodni A. A., 2007]

The selectivity is a widely used characteristic of ion exchange systems. It shows the choice of the material to one ion in comparison with another ion. The selectivity is a comparative value. The easiest definition of selectivity can be done by comparing the equivalent fractions of the ion in two phases. The exchanger is considered as selective towards one ion, if (at the equilibrium state) the equivalent fraction of this ion in the exchanger phase is higher than in the surrounding solution. Such a special selection characteristic usually depends on the problem to be solved and on experimental data available [Zagorodni A. A., 2007].

In the presence of confounding processes (such as chemisorption, microbial degradation, precipitation, and steric effects), selectivity coefficients can be used to generate exchange isotherms utilizing a reverse order to the usual procedure [Bloom S. A. and Mansell R. S., 2001].

## Author details

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