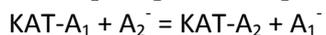
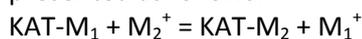


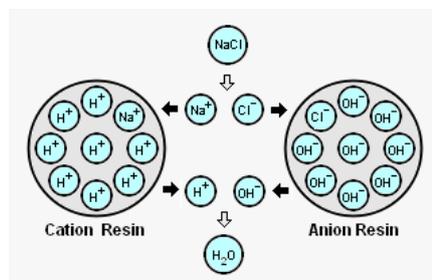
## 9. Determination of NaCl using ionic exchangers

**Ionic Exchange** is the process of exchange of mobile ions into other ions bearing the same sign, which occur on special resins. Cations are exchanged in cation resins, anions – in anion resins. The combination of these resins, cation and anion, allows to demineralize water; this is possible if all cations are exchanged by  $H^+$  ions, while all anions – by the  $OH^-$ . The result is chemically pure water. Such processes are widely applied in technology, but also in everyday's life: there are home water purification and demineralization units.

The process of ionic exchange can be schematically presented as follows:



where: KAT– cation resin skeleton; AN– anion resin skeleton;  $M_1^+$ ,  $M_2^+$  – the cations exchanged;  $A_1^{n-}$ ,  $A_2^{n-}$  – the anions exchanged;  $M_1$ ,  $M_2$  – active center of cation resin containing exchanged ions;  $A_1$ ,  $A_2$  – active center of anion resin containing exchanged ions.



*The scheme of simultaneous exchange in mixed deposit (like in home demineralizers).*

The exchange proceeds in stages:

- transfer of ions from the bulk solution towards the surface of the resin,
- transfer of ions inside the grain of resin towards the exchanging group,
- chemical reaction (double exchange),
- transfer of exchanged ions inside the grain towards its surface,
- detachment of the exchange ion from the surface and its migration towards the bulk solution,

The movement of ions from the bulk solution towards the surface of the resin and vice versa through the interphase layer is known as external diffusion. Transport of ions inside the resin is named internal diffusion.

The total rate of the exchange process is governed by the rates of the individual stages. Of course, the slowest ones are influencing it most of all – these are the internal and external diffusion processes. They depend mainly on the structure of resin (higher cross-linking degree decreases the external diffusion rate), but also on temperature, viscosity of the liquid etc.

**Ionic exchangers**, known also as ions exchanging resins, are water-insoluble and are able to exchange positively or negatively charged ions in solution into equivalent amounts of mono-charged ions which are contained in the resins. They are divided into:

- cation resins (exchange cations, their character is similar to salts or is acidic). They can be neutral or slightly acidic, when containing weakly dissociated functional groups ( $-OH$ ,  $-COOH$ ,  $-SH$ ,  $-CH_2SH$ ). Or are more acidic, able to exchange all the cations, with strongly dissociated groups ( $-SO_3H$ ,  $-CH_2SO_3H$ );
- anion resins (exchange anions, their character is similar to salts or is alkaline).

The main notions are:

**Exchange capacity** – this is the number of milliequivalents of the exchanged ions per the unit of mass (g) or volume ( $dm^3$ ). The exchange capacity is proportional to the number of functional groups in the resin and inversely proportional to the degree of cross-linking of the resin's skeleton.

**Column breakthrough point** – is the moment in the exchange process when concentration of the exchanged ion in the solution passing the column reaches the value assumed as critical. Attainment of this point means the necessity of the regeneration of the column (cleaning which leads to restoring the initial exchanging ability of the resin).

**The cycle of the exchange:**

- Preparation of the deposit (ionic exchangers are sold dry, before the first use they should be swelled). In our exercise this point is needless.
- The exchange, not longer than to the column breakthrough point.
- Regeneration and rinsing the deposit.

In our exercise we will exploit the phenomenon of the ionic exchange for determination of salt (NaCl) content by the acid-base titration. We will use cation resin, which will be regenerated using 2M HCl and after that will exchange stoichiometrically (i.e. completely) the cations  $\text{Na}^+$  into  $\text{H}^+$ . In effect, after passing the column, the solution of NaCl will be converted to HCl, which can be easily analyzed quantitatively using NaOH solution of known concentration as titrant. Of course, one can also use anion exchanger to convert  $\text{Cl}^-$  ions into  $\text{OH}^-$ , which can be analyzed using a strong acid as titrant as well.

### Chemicals and equipment

1. NaOH solution of known concentration (already prepared – Task 008);
2. Phenolphthalein (indicator);
3. 2M HCl (look for the bottles in main lab);
4. Beakers, Erlenmeyer flasks;
5. The glass column with cation resin

### Procedure

**Attention:** During regeneration, as well as during the exchange procedure, the rate of leakage from the column should be equal to 2-3 drops per second. Too fast leakage means incomplete exchange, resulting in an error of the analysis. The resin in column should be always covered by liquid. Do not allow the resin to have contact with air. If this happens, ask the teacher – the deposit has to be deaerated, the rinsing and exchange procedure should be repeated!

1. **Regeneration of the column:** Pass 100 ml 2M HCl solution through the column, and next 400 mL of distilled water. Check the eluent – if not neutral (red litmus paper), pass additional portion of water. Such regeneration will be sufficient for 5 exchanges.
2. **Preparation of weighed portions:** The mass is calculated in such the way that further titration will require 15-25 mL of our titrant. We assume the reaction scheme is  $\text{KAT-H}^+ + \text{MeCl} \rightarrow \text{KAT-Me}^+ + \text{HCl}$ , and the solution after exchange will be titrated using the NaOH solution prepared in Task 008. Moreover we assume that NaCl (or KCl) is only 50% of the total mass of the sample – so, the mass of NaCl or KCl calculated from the reaction stoichiometry has to be multiplied by 2. Further weighed portions will be prepared after the first, control titration; their masses have to be corrected to achieve the titrant volume 15-25 mL (too low volume means higher error of the volume reading, too high volume causes superfluous consumption of the titrant).
3. **Ionic exchange:** Transfer the weighed portion quantitatively (rinsing remains with the wash bottle) to a small beaker and dissolve it in ca. 20mL of distilled water. Pour solution carefully to the column, rinse the remains to it. Pass the sample through the column and next also ca. 100 mL of water. Collect the effluent in Erlenmeyer flask.
4. **Titration:** Titrate the effluent using your NaOH titrant, with phenolphthalein as indicator (other indicators are also acceptable if fitted to the pH jump in titration curve, for instance methyl red).
5. The procedure (points 2-4) should be performed at least 3 times

### Calculations and report

The final report should contain masses of the weighed portions, the respective volumes of titrant, calculated masses of NaCl or KCl and the content of this salt in the samples expressed as weight%. Finally, calculate the arithmetic mean weight% of salt in the total sample.

Sources:

[http://www.filtertech.com.pl/artykuly/wymiana\\_jonowa\\_-\\_podstawowe\\_informacje](http://www.filtertech.com.pl/artykuly/wymiana_jonowa_-_podstawowe_informacje)

[http://en.citizendium.org/wiki/Condensate\\_polishing](http://en.citizendium.org/wiki/Condensate_polishing)

textbooks