THEORETICAL MODEL OF SEPARATION OF ISOTOPES DURING PROCESS OF CRYSTALLIZATION

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Quasi-equilibrium mode of sedimentation.

Let us consider separation of isotopes at evaporation of the saturated solution on an example of separation of isotopes of chlorine at sedimentation of NaCl (halite). At first we shall consider "quasi-equilibrium" mode of sedimentation, at which at each moment of sedimentation the equilibrium (chemical and isotope) between a solution and *surface* of a crystal phase is established. As is known, the majority of crystals at enough slow speed of sedimentation crystallize in this mode [1]. Below we shall show, what changes can bring the account of kinetic factor.

If saturated salt solution contains $n^{\mathrm{H_2O}}$ mole of water and n_{aq}^{NaCl} moles of salt, mole ratio $\frac{n_{aq}^{\mathrm{NaCl}}}{n^{\mathrm{H_2O}}} = s\left(T\right)$ is determined by salt solubility. Thus the dissolved salt consists of ${}^{35}n_{aq}$ moles of $\mathrm{Na^{35}Cl}$ and ${}^{37}n_{aq}$ moles of $\mathrm{Na^{37}Cl}$, ${}^{35}n_{aq} + {}^{37}n_{aq} = n_{aq}^{\mathrm{NaCl}}$.

As water evaporates, the sedimentation of crystal phase begins, in each moment of it

$$n_{aq}^{\mathrm{NaCl}} = s\left(T\right) n^{\mathrm{H_2O}} = s\left(T\right)\left(n_0^{\mathrm{H_2O}} - n_{evap}^{\mathrm{H_2O}}\right),$$

$$n_{solid}^{\mathrm{NaCl}} = s\left(T\right) n_{evap}^{\mathrm{H_2O}},$$

where $n_0^{\mathrm{H_2O}}$ is initial amount of water, $n_{evap}^{\mathrm{H_2O}}$ is amount of evaporated water.

The ratio between $\mathrm{Na^{35}Cl}$ and $\mathrm{Na^{37}Cl}$ in a superficial layer of a solid phase which is in direct contact to a solution, at each moment is determined by isotope separation factor α; the internal space of a crystal does not exchange with a solution due to extremely low speed of diffusion of ions in solid salts [2].

Let in equilibrium conditions has evaporated dn_{evap} of water. Then $dn_{solid}^{\mathrm{NaCl}} = s\left(T\right) dn_{evap}$ of salt has sedimented. Accordingly, solution lost $dn_{aq}^{\mathrm{NaCl}} = -s\left(T\right) dn_{evap}$. As

$$\begin{gathered} d^{35}n_{solid} + d^{37}n_{solid} = dn_{solid}^{\mathrm{NaCl}} = s\left(T\right) dn_{evap} \\ d^{35}n_{aq} + d^{37}n_{aq} = dn_{aq}^{\mathrm{NaCl}} = -s\left(T\right) dn_{evap} \end{gathered}$$

and by definition the separation factor (in the assumption of uniformity of structure of a liquid phase) is equal

$$\alpha_{35/37} = \frac{d^{35}n_{solid} \left/ d^{37}n_{solid}\right.}{{}^{35}n_{aq} \left/ {}^{37}n_{aq}\right.},$$

we have

$$d^{35}n_{solid} = \frac{{}^{35}n_{aq}}{{}^{37}n_{aq}} \cdot \alpha_{35/37} \cdot d^{37}n_{solid}.$$

Because ${}^{35}n_{aq} = {}^{35}n_0 - {}^{35}n_{solid}$ and is similar for an isotope ${}^{37}\mathrm{Cl}$, we have the equation with separated variables, known in the theory of co-crystallization:

$$\frac{d^{35}n_{solid}}{{}^{35}n_0 - {}^{35}n_{solid}} = \alpha_{35/37} \cdot \frac{d^{37}n_{solid}}{{}^{37}n_0 - {}^{37}n_{solid}}. \tag{1}$$

Integration of (1) gives the equation similar to Doerner-Hoskins formula [1] which describes the co-crystallization in quasi-equilibrium mode:

$$\ln\left(1-\frac{{}^{35}n_{solid}}{{}^{35}n_0}\right)=\alpha_{35/37}\cdot\ln\left(1-\frac{{}^{37}n_{solid}}{{}^{37}n_0}\right). \qquad (2)$$

This equation should be solved taking into account that ${}^{35}n_{solid}+{}^{37}n_{solid}=s\left(T\right)\cdot n_{evap}$, where n_{evap} is amount of evaporated water. Solution of (2) gives the dependence of amount of isotopes ^{37}Cl and ^{35}Cl in a solid phase as function of n_{evap}. It, in turn, allows us to calculate the isotope relation in a superficial layer of a crystal, and further to calculate δ^{37}Cl in superficial layer of a crystal and in stock solution as functions of n_{evap}:

$$\delta^{37}\mathrm{Cl}_{solid}=1000\cdot\left(\frac{d^{37}n_{solid}/d^{35}n_{solid}}{\mathrm{SMOC}}-1\right),\quad \delta^{37}\mathrm{Cl}_{aq}=1000\cdot\left(\frac{d^{37}n_{aq}/d^{35}n_{aq}}{\mathrm{SMOC}}-1\right).$$

Here SMOC ("Standard mean ocean chloride") is relation of concentration ${}^{37}\mathrm{Cl}/{}^{35}\mathrm{Cl}=0.324$ in ocean water accepted as the standard.

It is possible to calculate dependence of $\delta^{37}\mathrm{Cl}_{solid}$ on depth of the salt stratum if it is known initial (at the moment of saturation) depth of a reservoir and area of its surface. If on unit of a surface of a reservoir $n_{solid}^{\mathrm{NaCl}}=s\left(T\right)n_{evap}^{\mathrm{H_2O}}$ moles of salt was sedimented, the height of a salt deposit will be

$$h=\frac{s\left(T\right)n_{evap}^{\mathrm{H_2O}}}{\rho},$$

where ρ is expressed in moles on unit of volume of solid NaCl and is equal to $0.03704479\ mole/cm^3$.

If $\left(s/s'\right)f$ of solid salt is greater than $\left(s/s'\right)f$ for hydrated ion, then during the process of sedimentation of salt from a solution the crystal is enriched by heavy isotope, and solution, on the contrary, by light isotope. The sedimentation of heavy isotope occurs non-uniformly — namely, the lowermost layers sedimented first should be enriched with heavy isotope to the greatest degree. If the structure of an initial solution corresponded to SMOC, the lowermost layer of salt should have enrichment of

$$\left(\delta^{37}\mathrm{Cl}_{solid}\right)_{bottom}=1000\cdot\left(\frac{1}{\alpha}-1\right).$$

As a result, most (approximately 2/3) part of salt stratum should be enriched with a heavy isotope. On the contrary, the uppermost layer of salt at exhausting evaporation should be considerably enriched with light isotope.

Diffusion mode of sedimentation.

Because the halite sedimentation occurs at nonzero speed, it is necessary to take into account the corrections caused by diffusion in the process of sedimentation. This question is considered by us in detail in the previous work. Here we remind the basic results. It is possible to consider separation of isotopes in the process of sedimentation of a crystal from saturated solution containing two or more isotopes of an element as a special case of co-crystallization.

It is known [1] that quantitative characteristic of co-crystallization is a degree of co-crystallization x, which is equal to relation of mass of an impurity caught by solid phase, to the mass of this impurity in initial solution. The degree of co-crystallization is usually expressed by differential factor of co-crystallization K_{diff}, which characterizes a degree of transition of co-crystallized component from initial environment in a layer of a solid phase. If y and ρ are mass and density of a deposit, accordingly, and V is a volume of environment, then

$$K_{diff}=\frac{\rho V}{\left(1-x\right)}\frac{dx}{dy}.$$

Value of K_{diff} depends upon degree of supersaturation of a solution, intensity of hashing, temperature and other factors.

For separation of isotopes during crystallization instead of factor of co-crystallization it is necessary to use differential factor of separation of isotopes α which is equal

$$\alpha_{35/37} = \frac{d^{35}n_{solid} \big/ d^{37}n_{solid}}{{}^{35}n_{aq} \big/ {}^{37}n_{aq}}.$$

Let us consider the sedimentation of any of isotopes, for example, ^{35}Cl. As $x = \frac{{}^{35}m_{solid}}{{}^{35}m_0} = \frac{{}^{35}n_{solid}}{{}^{35}n_0}$, where m_0 and n_0 are initial mass and amount of an isotope in the system, then differential factor of co-crystallization for this isotope can be presented as

$${}^{35}K_{diff} = \frac{\rho_{solid} V_{aq}}{(1-x)}\frac{dx}{dy} = \frac{\rho_{solid} V_{aq}}{\left(1 - \frac{{}^{35}n_{solid}}{{}^{35}n_0}\right){}^{35}n_0}\frac{d^{35}n_{solid}}{dy} = \frac{\rho_{solid} V_{aq}}{{}^{35}n_{aq}}\frac{d^{35}n_{solid}}{dy}. \qquad (3)$$

For sedimentation of other isotope (^{37}Cl) we have similar equation and receive

$$\alpha_{35/37} = \frac{{}^{35}K_{diff}}{{}^{37}K_{diff}}. \qquad (4)$$

Equation (4) allows us to use results, received earlier in the researches on the phenomenon of co-crystallization, for analysis of separation of isotopes at crystallization from solutions.

In diffusional mode of sedimentation the layer of a liquid phase by thickness δ (diffusional layer) is formed at a surface of crystals. Time of ion transport through this layer is commensurable with growth speed of crystal, but quicker than the equilibrium distribution is established. For this mode the factor co-crystallization is expressed by the Barton-Prime-Slichter formula [1]:

$$K_{diff} = \frac{K_{eq}}{[K_{eq} + (1 - K_{eq})\exp(-\delta G / D)]}, \qquad (5)$$

where G is linear growth speed of crystal, D is factor of diffusion of ions in a liquid phase, K_{eq} is equilibrium factor of co-crystallization, describing co-crystallization in conditions of small speed of crystal growth (in quasi-equilibrium mode).

Coming back to the (4), we can rewrite the equation for equilibrium factor co-crystallization of isotopes as

$$\alpha^{eq}_{35/37} = \frac{{}^{35}K_{eq}}{{}^{37}K_{eq}}. \qquad (6)$$

Equations (4), (5), and (6) give

$$\alpha_{35/37} = \alpha^{eq}_{35/37}\frac{{}^{37}K_{eq} + \left(1 - {}^{37}K_{eq}\right)\exp\left(-\delta G / {}^{37}D\right)}{{}^{35}K_{eq} + \left(1 - {}^{35}K_{eq}\right)\exp\left(-\delta G / {}^{35}D\right)}. \qquad (7)$$

For practical usage of equation (7) it is necessary to express ${}^{35}K_{eq}$ and ${}^{37}K_{eq}$ using results on quasi-equilibrium mode of sedimentation described above. Because the volume of a phase, in which isotope exchange occurs (surface + near-surface layer) is small in comparison with volume of stock solution, one can neglect the change of isotope composition of a solution when considering the sedimentation of the next thin layer of a crystal. In this case the equilibrium factor of co-crystallization of light isotope will be equal

$${}^{35}K_{eq} = \frac{{}^{35}c_{solid}}{{}^{35}c_{aq}},$$

where c_{solid} and c_{aq} are concentrations of isotope in solid phase and in solution, accordingly. Taking into account these relations and obvious equality

$$\frac{{}^{35}c_{solid} + {}^{37}c_{solid}}{{}^{35}c_{aq} + {}^{37}c_{aq}} = S,$$

where S is determined by salt solubility, we have

$$\frac{{}^{35}K_{eq}{}^{35}c_{aq} + {}^{37}K_{eq}{}^{37}c_{aq}}{{}^{35}c_{aq} + {}^{37}c_{aq}} = S$$

. Further, taking into account the equation (6), we have

$${}^{37}K_{eq} = S\frac{{}^{35}c_{aq} + {}^{37}c_{aq}}{\alpha^{eq}_{35/37}{}^{35}c_{aq} + {}^{37}c_{aq}}, \quad {}^{35}K_{eq} = \alpha^{eq}_{35/37}S\frac{{}^{35}c_{aq} + {}^{37}c_{aq}}{\alpha^{eq}_{35/37}{}^{35}c_{aq} + {}^{37}c_{aq}}. \tag{8}$$

In approximation used by us $\frac{{}^{37}c_{aq}}{{}^{35}c_{aq}} = \mathrm{SMOC}$ ("standard mean ocean chloride"), and we can write

$${}^{37}K_{eq} = S\frac{1+\mathrm{SMOC}}{\alpha^{eq}_{35/37} + \mathrm{SMOC}}, \quad {}^{35}K_{eq} = \alpha^{eq}_{35/37}S\frac{1+\mathrm{SMOC}}{\alpha^{eq}_{35/37} + \mathrm{SMOC}}. \tag{9}$$

Substituting (9) in (7), we receive final expression for differential factor of separation of isotopes at sedimentation in diffusion mode:

$$\alpha_{35/37} = \alpha^{eq}_{35/37}\frac{SA + [1 - SA]\exp\left(-\frac{\delta G}{{}^{37}D}\right)}{\alpha^{eq}_{35/37}SA + \left[1 - \alpha^{eq}_{35/37}SA\right]\exp\left(-\frac{\delta G}{{}^{35}D}\right)}, \tag{10}$$

(here $A = \frac{1+SMOC}{\alpha^{eq}_{35/37} + SMOC}$). One can see from equation (10) that if growth rate of a crystal G approaches zero, separation factor approaches its meaning for quasi-equilibrium sedimentation $\alpha^{eq}_{35/37}$ (i.e., isotope fractionation is fully controlled by thermodynamics). In opposite case, when growth rate of a crystal is great, growing crystal exhaustively grasps ions from solution, and separation of isotopes does not occur ($\alpha = 1$). In intermediate cases various behavior of $\alpha_{35/37}$ can occur. It should be noted that always $\frac{{}^{35}D}{{}^{37}D} > 1$, as light isotope migrates faster. If $(s/s')f$ of a solid phase is higher than $(s/s')f$ of aqua complex, the thermodynamic isotope effect favors concentration of heavy isotope in solid phase. Thus, kinetic (diffusion) and the thermodynamic factors in such case work in opposite directions, that should result in extremal character of dependence of differential factor of separation of isotopes from speed of sedimentation.

The dependence of separation factor from δG product is given in Fig. 1. As it is visible in the figure, with growth of speed of sedimentation the value of $\alpha_{35/37}$ at first increase from initial equilibrium value $\alpha^{eq}_{35/37}$ and approaches a maximum.

At this speed the influence of kinetic factor is maximal. It is visible also, that the logarithm of separation factor changes its sign, that is, at high speeds of sedimentation (high values of product δG) the direction of separation of isotopes reverses, and the crystal should be enriched by light isotope. Such enrichment in natural samples of salts usually is not observed, whence it is possible to conclude, that the separation of isotopes at sedimentation is caused (or at least controlled) mainly by thermodynamic reasons.

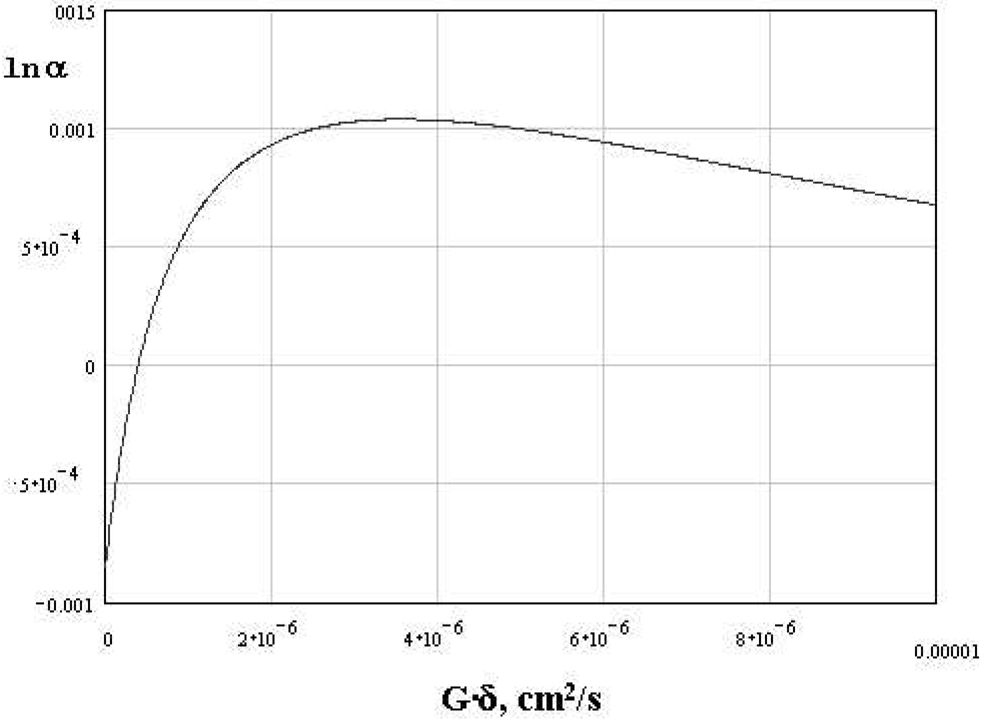

Figure 1: Dependence of differential separation factor of isotopes of chlorine in the process of sedimentation upon the speed of growth of solid phase.

Adsorption-kinetic mode of sedimentation.

At sedimentation from strongly supersaturated solution at intensive hashing the growth rate of crystals is commensurable with speed of migration of ions in near-surface layer and with speed of the reaction of crystallization, but less than speed of moving of ions in the solution (adsorption-kinetic mode of sedimentation). Obviously, however, that in the nature at evaporation of water reservoirs the intensive hashing has no place, and consequently sedimentation occurs or in quasi-equilibrium (at small speed of evaporation), or in diffusional mode. Therefore it is possible not to consider the adsorption-kinetic of sedimentation at all.

There are also other serious reasons not to consider the adsorption-adsorption-kinetic and other similar mechanisms of sedimentation. As has been shown in the experimental works on study of growth of crystals from a solution performed recently [3, 4], the growth of crystals is always essentially non-equilibrium process. In the works mentioned is was shown that in process of sedimentation in system solution — crystal the dissipative structures are always formed which lead to formation of flows of a solution around of crystal. As the consequence, at any mode of sedimentation the diffusion layer δ is always formed near the crystal surface. This circumstance, apparently, explains the fact that the Barton-Prime-Slichter equation describes co-crystallization in the large number of cases.

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