STUDY OF THE COCRYSTALLIZATION OF NICKEL ION WITH MAGNESIUM AMMONIUM SULFATE USING $^{63}$Ni TRACER

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(Received January 3, 1972)

The cocrystallization of nickel ammonium sulfate with magnesium ammonium sulfate has been studied at low concentrations of the nickel salt, using radiotracer $^{63}$Ni. The applicability of the equations developed by BERTHELOT and NERNST, DOERNER and HOSKINS, and ABU ELAMAYEM is discussed. It is concluded that only the logarithmic equation of Doerner–Hoskins holds good for this picromerite system. This reveals that during crystallization the crystals that separate are in momentary equilibrium with the mother liquor and hence the composition of the crystals separating is not homogeneous. Crystallization at higher temperature yields purer crystals of the magnesium salt.

Introduction

Fractional crystallization or cocrystallization in ternary systems involves non-equilibrium states, but they can be studied with the aid of theoretical equations developed for systems in equilibrium, or for the coprecipitation of impurities with a substrate. The homogeneous distribution law of BERTHELOT and NERNST\(^1\) is as follows:

$$\frac{x}{y} = D \frac{a - x}{b - y}$$  \hspace{1cm} (1)

where \(a, b\) – total amounts of the original salts,
\(x, y\) – amounts in the solid phase,
\((a - x), (b - y)\) – amounts in the liquid phase,
\(D\) – distribution constant.

A logarithmic relation has been developed by DOERNER and HOSKINS\(^2\) for the coprecipitation of radium and barium chlorides with sulfuric acid:

$$\ln \frac{y}{a} = \lambda \ln \frac{n}{b}$$  \hspace{1cm} (2)

where \(a, b\) – initial amounts,
\(y, n\) – final amounts of radium and barium chlorides in solution,
\(\lambda\) – constant.
ABU ELAMAYEM recently derived Eq. (3) for the fractional crystallization of isomorphous salts in a non-equilibrium system:

\[
- \frac{dy}{dw} = \frac{1}{w} \left( \frac{1}{1 + \frac{M_B}{M_A} \left( \frac{1 - w}{K (a - wy) - 1} \right) M_A^{1/m} - y} \right)
\]

where

- \( w \) — fraction by weight of the original mixture separated as crystals,
- \( y \) — fraction by weight of the less soluble salt in the crystals,
- \( a \) — fraction by weight of the less soluble salt in the initial mixture,
- \( M_A, M_B \) — molecular weights of the two salts,
- \( K, m \) — constants defined by the semiempirical equation of HILL et al.:

\[
\frac{R_1}{R_s^m} = K
\]

where \( R_1, R_s \) — mole ratios of salts A and B in the liquid and solid phases, respectively,
- \( m \) — empirical constant,
- \( K \) — distribution constant.

Eqs (1) and (2) have been extensively used by many workers in both coprecipitation and fractional crystallization studies at all impurity concentrations. While CHLOPIN uses the Berthelot-Nernst law for the coprecipitation of radium nitrate with barium nitrate, CALLOW invokes the Doerner-Hoskins law to explain the behaviour of the fractional crystallization of lanthanides as double ammonium nitrates. Both workers have carried out experiments with varying concentrations of the ‘impurity’, and CALLOW has even applied Eq. (2) for industrial separations.

The authors have reported on the application of the above equations to the picromerite system:

\[
\frac{\text{Ni}}{\text{Mg}} (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}
\]

where the nickel compound is the less soluble salt. Preliminary investigations at \( a = 0.333 \) and then at \( a = 0.909 \) to 0.0476 revealed that \( \lambda \) and \( D \) calculated from the experimental results were not constant, showing that Eqs (1) and (2) are not valid for this system at these concentrations. However, it was found that Eq. (3) was of practical importance. With a proper choice of values for the parameters \( K \) and \( m \), it can be solved by Euler’s method of successive approximations and the amount of the less soluble salt crystallizing out of the ternary system can be theoretically computed \( (y_{\text{theor}}) \). It was seen that the values of \( y_{\text{theor}} \) were in good agreement with \( y_{\text{expt}} \).