THE CRYSTALLISATION OF ALKALINE-EARTH METAL TUNGSTATES FROM SOLUTIONS IN SODIUM TUNGSTATE MELTS

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LIST OF SYMBOLS

a = (= dC/dT) change of solute concentration with respect to temperature
A = area
C = solute concentration
C_i = initial solute concentration
C_e = eutectic concentration
C_o = solute concentration at initial starting temperature
C_{sat} = saturation solute concentration
C_t = solute concentration at any time
C = solute concentration at induction period
D = diffusion coefficient
f_s = shape factor
ℓ = crystal length
ℓ_{av} = average crystal length
$(\ell_{av})_{fin}$ final average crystal length
ℓ_{fin} = final maximum crystal length
ℓ_t = maximum crystal length at any time
k_{D_ℓ} = diffusion rate constant for crystal length
k_{D_w} = diffusion rate constant for crystal width
N = nucleus number
R_C = rate of mixing
R_S = (= dS/dt) rate of development of supersaturation
R_T = (= dT/dt) rate of cooling
S = supersaturation
S = supersaturation at induction period
t = time
$\bar{t}$ = induction period
T = temperature
T_i = initial temperature
T_f = final temperature
T_o = initial starting temperature

T_x = crystallisation temperature

$\bar{T}$ = induction temperature
w = crystal width
w_{av} = average crystal width

$(w_{av})_{fin}$ = final average crystal width

w_t = maximum crystal width at any time
w_{fin} = final maximum crystal width

W = crystal weight

α = extent of crystallisation
δ = crystal thickness
ρ = crystal density
η = viscosity
ϕ = porosity
τ = growth time after induction period
ρ_{soln} = density of solution

ABSTRAK

Kerja ini mengemukakan suatu kajian mengenai penghabluran Tungstat Logam Alkali-Bumi dari larutan lebur Natrium Tungstat.

Keterlarutan Garam-Garam Logam Alkali-Bumi pada suhu-suhu yang berbeza antara 600° ke 1200°C telah didapati dari bahan bacaan yang tertentu.

Kajian kuantitatif peringkat awal mengenai penghabluran Titanat Logam Alkali-Bumi dibuat dengan cara penyejukan perlahan yang berterusan kepada larutan tepu lebur Logam Klorid Alkali-Bumi dari suhu pengabluran awal, $T_o = 1000^{\circ}$ ke 1200°C, ke takat suhu ambien. Kesan suhu penghabluran awal dan keterlarutan zat larutan suhu penghabluran awal(saling tindakan zat larutan-pelarut) dan kadarcepat penyejukan atas bentuk hablur ahkir dikaji. Hasil kajian ini dibanding dengan hasil kajian peringkat awal mengenai penghabluran Tungstat Logam Alkali-Bumi dengan cara penyejukan perlahan berterusan kepada larutantepu lebur Tungstat Natrium dari suhu-suhu penghabluran awal, $T_o = 800^{\circ}$ ke 1000°C, ke takat suhu ambien. Tungstat Natrium digunakan sebagai pelarut yang sesuai bagi penghabluran Tungstat Logam Alkali-Bumi dalam lingkungkan bezantara suhu $T_o = 800^{\circ}$ ke 1000°C dan kadar-kadar penyejukan $R_T = 40^{\circ}$ ke 200°C sejam.

Penghabluran Tungstat Kalsium, Stronsium dan Barium dari lebur Tungstat Natrium dikaji, dengan teliti melalui dua cara: iaitu, penghabluran dalam mangkuk alumina dengan cara penyejukan berterusan perlahan dan penghabluran dalam mangkuk platinum dengan cara penyejukan berterusan perlahan.

Bagi penghabluran dalam mangkuk alumina, tumbesar hablur pada amnya berlaku hampir selepas penyejukan bermula. Walaupun tidak ada kala induksi tetapi tungstat Stronsium dan Barium menunjukkan tumbesar perlahan pada peringkat awal untuk penghabluran pada $T_o = 800^{\circ}C$ dan $R_T = 40^{\circ}C$ sejam. Barangkali pada kala tumbesar perlahan, sedikit ketepuan lampau berlaku dan mungkin peroses membentuk nukleus dan sedikit tumbesar pada nukleus-nukleus halus awal kedua-duanya terjadi dengan serentak.

Pada nilai rendah α ($\alpha \leq 0.1$), panjang hablur (ℓ) berubah secara linear dengan masa (t). Keputusan-keputusan ini memberi saranan bahawa tumbesar sistem-sistem ini mungkin pembauran kadarcepat-terkawal. Balam semua kes di atas anisometri hablur tidak berubah. Beberapa perhubungan teoretis telah dicadang untuk menuntukan angkatap kadarcepat eksperimen didapati bertambah mengikut susunan:

$$CaWO_4 < SrWO_4 < BaWO_4.$$

Untuk penghabluran dalam mangkuk platinum, tumbesar hablur pada amnya berlaku selepas suatu kala induksi yang singkat. Pada kala induksi seperti ini ketepuan lampau berlaku dan mungkin peroses membentuk nukleus-nukleus dan sedikit tumbesar pada nukleus-nukleus halus awal kedua-duanya terjadi dengan serentak. Perbezaan nombor nukleus (N) dan nilai-$\bar{t}$ dengan suhu penghabluran awal (T_o) dan kadar penyejukan (R_T) dikaji dengan teliti. Nilai-$\bar{t}$ bertambah dengan kekurangan dalam kadar penyejukan.

Angkatap kadarcepat bagi tumbesar hablur $CaWO_4$, $SrWO_4$ dan $BaWO_4$ agak kecil dari nilai anggaran.

ABSTRACT

This work presents a study of the crystallisation of Alkaline-earth Metal Tungstates from solutions in Sodium Tungstate Melts.

The solubilities of the Alkaline-earth Metal Salts in Sodium Tungstate at various temperatures from 600° to 1200° C were obtained from the literature.

Preliminary quantitative studies were made on the crystallisation of Alkaline-earth Metal Titanates by slow continuous cooling of saturated solutions in Alkaline-earth Metal Chloride Melts from initial crystallisation temperatures, $T_o = 1000°$ to $1200°$ C, down to ambient temperature. The effects of initial crystallisation temperature and solute solubility at the initial crystallisation temperature (solute-solvent interaction) and the rate of cooling on the final crystal form and size were investigated. These results were compared with the results of the preliminary studies on the crystallisation of Alkaline-earth Metal Tungstates by slow continuous cooling of saturated solutions in Sodium Tungstate Melts from initial crystallisation temperatures, $T_o = 800°$ to $1000°$ C, down to ambient temperature. Sodium Tungstate was a suitable solvent for crystallisation of the Alkaline-earth Metal Tungstates within the temperature range $T_o = 800°$ to $1000°$ C and rates of cooling $R_T = 40°$ to $200°$ C/hr.

The crystallisation of Calcium, Strontium and Barium Tungstates from Sodium Tungstate Melts was studied in detail by two methods, viz. the crystallisation in alumina crucibles by slow continuous cooling, and the crystallisation in platinum crucibles by slow continuous cooling.

For crystallisation in alumina crucible, crystal growth generally occurred almost after the onset of cooling. Although there was no induction period but Strontium and Barium tungstates showed slow growth at the early stages for crystallisation at $T_o = 800^{\circ}C$ and $R_T = 40^{\circ}C/hr$. Perhaps during this period of slow growth some supersaturation developed and probably both nucleation and some growth onto very small early nuclei occurred simultaneously.

At low α-values($\alpha \leq 0.1$), crystal length (ℓ) varied linearly with time (t). These results suggest that the growth of these systems was probably diffusion rate-controlled. In all the above cases, crystal anisometry did not change. Some theoretical relations have been proposed for the determination of rate constants. The experimental rate constants increased in the order:

$$CaWO_4 < SrWO_4 < BaWO_4 .$$

For crystallisation in platinum crucible, crystal growth generally occurred after a short induction period. During such induction periods supersaturation developed and probably both nucleation and some growth onto very small early nuclei occurred simultaneously. The variation of nucleus number (N) and $\bar{t}$ - values with initial crystallisation temperature (T_o) and rate of cooling (R_T) was studied in some detail. $\bar{t}$ - values increased with decrease in rate of cooling.

The rate constants for crystal growth of $CaWO_4$, $SrWO_4$ and $BaWO_4$ were much smaller than the estimated values.

INTRODUCTION

INTRODUCTION

GENERAL

New materials for use as ceramics, refractories, dielectrics, and engineering materials have been prepared in recent years by crystallisation.(1-6) Alkaline-earth metal tungstates are an important group of such materials; the crystals are used in various optical and other physical applications.(7-9)

Alkaline-earth metal salts of the type MXO_4 have been crystallised by aqueous precipitation, (10-11) and hydrothermal crystallisation.(12-13) These methods produced very small crystals (in some cases of uncertain composition) and are, therefore, not very useful. The most suitable method is crystallisation from solutions in metal salt melts, at quite low temperatures, down to 1000 °C below the fusion temperature of the solute; the solvents used for such crystallisation include alkali metal halides, alkaline-earth metal halides, sodium salts of the oxy-anion. (14-15)

The crystallisation of metal salts and oxides from melts has been reviewed by Laudise (16) , Kröger (17), White (18) and Schroeder (19) . Survey of the literature, however, shows very few quantitative studies on the effects of different crystallisation conditions on the final crystal size and other properties of the crystallised materials. The kinetics and mechanism of such crystallisations have been studied by only a few workers.(20-22)

The present work is mainly concerned with the kinetics of crystallisation of Alkaline-earth metal tungstates from Sodium tungstate melts at different temperatures and rates of cooling.

I. PHYSICAL CHEMISTRY OF MOLTEN SALT MIXTURES

A. ELECTROSTATIC INTERACTION AND STRUCTURE

Alkaline Metal Halide Melts: When a metal salt crystal is melted its cations and anions disperse. The cohesive force between the ions is primarily related to the Coulombic interactions of the positive and negative spherical charge distributions. At the equilibrium state the total attractive force must be balanced by a repulsive force. In all theories, these forces are more or less arbitrarily introduced as short-range functions. A stable structure results when each anion is adjacent to a number of cations, and vice versa.

Alkali-Metal halides: Molten salts of the type A^+X^- may be described by a simple quasi-lattice model.(23) This quasi-lattice consists of two sub-lattices ___ one of cations and the other of anions ___ which interlock so that the anions have cations as nearest neighbours and the cations have anions as nearest neighbours. According to this model the structure of molten salt of the type A^+X^- is similar to the structure of NaCl crystals.(23)

Melt structures can be described more exactly by the "Hole Theory". This theory describes the spontaneous density fluctuations of the ions as the constituent particles move about under thermal agitation. Even in the unmelted crystal such density fluctuation occurs at elevated temperatures by the motion of unoccupied lattice sites or missing particles. Motion of unoccupied lattice sites occurs by a shift of a particle in the crystal into a neighbouring unoccupied site. In a liquid, the situation is much less restrictive and extra freedom of particle movement occurs.

Alkaline-earth metal halides: The structures of melts of salts of the type BX_2 have not been reported. These are probably similar to the structure of BX_2 crystals.(24) In such structures, each B^{2+} ion is surrounded by eight X^- ions at the corners of a cube, and each X^- ion by four B^{2+} ions at the corners of a regular tetrahedron.

Metal oxy-anion salts: The structures of melts of metal oxy-anion salts ($A_2^{++}Y^{--}$ or $B^{++}Y^{--}$) have not been reported. These may also be similar to the structures of the crystals.

Molten Salt Mixtures

$A^+X^- - B^+X^-$ mixtures are the simplest types of binary ionic solutions. They were studied by Kleppa (25), and Kleppa and Hersh (26). Schematically the structure can be represented as follows:-

$$\begin{array}{cccccc}
A^+ & X^- & B^+ & X^- & A^+ & X^- \\
X^- & A^+ & X^- & B^+ & X^- & A^+ \\
A^+ & X^- & B^+ & X^- & A^+ & X^- \\
X^- & B^+ & X^- & A^+ & X^- & B^+
\end{array}$$

In such mixtures, the cations all have the same immediate environment of anions as in the pure components. Ionic interactions will diminish fairly rapidly with distance, and the energy change during mixing must be mainly due to interactions between next-nearest neighbours. If this energy of interaction is not too strong the tendency for maximization of entropy will cause the two types of cations to be almost "randomly distributed" amongst the cation sites. In a mixture of a - moles of AX and b - moles of BX, the chance of any A^+ ion having another A^+ ion as a particular one of its nearest cations is $\left[\frac{a}{a+b}\right]$, and the chance of this neighbouring cation being a B^+ cation is $\left[\frac{b}{a+b}\right]$.

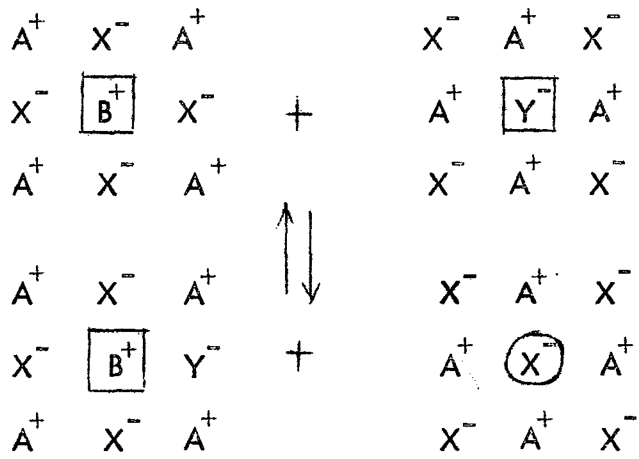
With aA^+ cations present, the number of A-B contacts is, therefore, proportional to (ab/a+b). The number of interactions between a cation and a distant unlike cation at any specified degree of removal is similarly proportional to (ab/a + b).

AX - BX_2 : Studies on AX - BX_2 mixtures have not been described in literature.

A^+X^- - B^+Y^- mixtures have been studied by Kleppa,(26), Flood, Forland and Grjotheim(27). In a melt of solvent, A^+X^- with solute B^+Y^-, the following equilibrium is set up:

$$A^+X^- + B^+Y^- \rightleftharpoons A^+Y^- + B^+X^-$$

This equilibrium can be represented schematically as follows:



$A^{+}X^{-}$ - $B^{++}Y^{--}$ mixtures: No work on the structures of mixed melts of alkaline-earth metal oxy-anion salts with alkali halides has been reported. These melts are also probably random mixtures that result from an equilibrium :

$$2A^{+}X^{-} + B^{++}Y^{--} \rightleftharpoons B^{++}X_2^{-} + A_2^{+}Y^{--}$$

B. THERMODYNAMICS OF BINARY MOLTEN SALT MIXTURES

General

If two substances, solvent A of mole-fraction x_A and solute B of mole-fraction x_B are mixed together at any temperature to give a non-ideal mixture then the chemical potential (μ_A) of the solvent is

$$\mu_A = \mu_A^\circ + RT\ln(a_A) = \mu_A^\circ + RT\ln(\gamma_A x_A) \qquad (1)$$

and the chemical potential (μ_B) of the solute is

$$\mu_B = \mu_B^\circ + RT\ln(a_B) = \mu_B^\circ + RT\ln(\gamma_B x_B) \qquad (2)$$

where,

μ_A° is the standard chemical potential of A

μ_B° is the standard chemical potential of B

a_A is the activity of A = $\gamma_A x_A$

a_B is the activity of B = $\gamma_B x_B$

γ_A and γ_B are the activity coefficients of A and B.

The Gibb's free-energy of mixing is given by

$$\Delta G_m = RT(x_A \ln\gamma_A x_A + x_B \ln\gamma_B x_B) \qquad (3)$$

For an ideal solution

$$\Delta G_m^{ideal} = RT(x_A \ln x_A + x_B \ln x_B) \qquad (4)$$

Then the excess Gibb's free energy of mixing is

$$\Delta G_m^E = \Delta G_m - \Delta G_m^{ideal}$$

$$= RT\,(x_A \ln \gamma_A + x_B \ln \gamma_B) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

For the solute, the excess chemical potential is

$$\mu_B^E = RT \ln \gamma_B$$

High negative ΔG_m^E values correspond to marked deviations from ideality and low γ_B (and/or γ_A) values.(23)

Saturated solutions

Saturated solution is attained —— at any temperature well below the solute melting point (T_m) —— when the following equilibrium is established:

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

At the equilibrium the chemical potentials of the solute in the saturated solution and in solid are equal; then

$$\mu^{\ell} = \mu^{s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where,

μ^{ℓ} = chemical potential of solute in the saturated solution

μ^{s} = chemical potential of solute in solid.

For ideal conditions, the difference between the chemical potential of pure liquid solute (B) and the solute in the solution is given by :

$$\mu_B^{l} = \mu_B^{o} + RT\ln x_B \qquad \text{...(7)}$$

where,

μ_B^{o} = standard chemical potential of solute (B) at any temperature

x_B = mole-fraction of the solute.

Combining equations (6) and (7),

$$\mu_B^{s} = \mu_B^{o} + RT\ln x_B \qquad \text{...(8)}$$

For the variation of the chemical potentials of pure solid and liquid with temperature, the following relation holds :

$$\frac{\partial}{\partial T}\left[\frac{\mu_B^{s} - \mu_B^{o}}{T}\right] = -\,\frac{H_B^{s} - H_B^{o}}{T^2} \qquad \text{...........(9)}$$

where,

H_B^{s} = enthalpy of solid solute (B)

H_B^{o} = enthalpy of liquid solute (supercooled to temperature, T)

Integrating equation (9),

$$\left[\frac{\mu_B^{s} - \mu_B^{o}}{T}\right]_{(T,P)} - \left[\frac{\mu_B^{s} - \mu_B^{o}}{T}\right]_{(T_M,P)} = -\int_{T_M}^{T} \frac{H_B^{s} - H_B^{o}}{T^2}\, dT$$

..............(10)

At any melting point pure solid and pure liquid are in equilibrium so that,

$$(\mu_B^{s})_{(T_M,P)} = (\mu_B^{o})_{(T_M,P)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Then the equation (10) becomes

$$\left[\mu_B^{s} - \mu_B^{o} / T\right]_{(T,P)} = \int_{T_M}^{T} \left[H_B^{s} - H_B^{o} / T^2\right] dT \quad \ldots\ldots\ldots\ldots(12)$$

Combining equations (8) and (12),

$$R \ln x_B = \int_{T_M}^{T} \left[H_B^{s} - H_B^{o} / T^2\right] dT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

$$= \int_{T_M}^{T} \Delta H_f / T^2 \, dT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

where,

ΔH_f = latent heat of fusion of the solute.

T near T_M

When the differences between the specific heats of solid and liquid forms of the same compound are usually much smaller than the latent heat of fusion, to a first approximation it may be assumed that ΔH_f is independent of temperature. Then the equation (14) becomes

$$R\ln(x_B) = -\Delta H_f\left[\frac{1}{T} - \frac{1}{T_M}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

that is the solubility depends solely on the latent heat of fusion of the solute and its melting point. The form of equation (15) is consistent with the empirical expression for the variation of solubility with temperature, i.e

$$\ln x_B = A - \frac{B}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

where,

$$A = \frac{\Delta H_f}{RT_M} \quad \text{and } B = \frac{\Delta H_f}{R}$$

Non-ideal solutions can be described in exactly the same way by including an activity-coefficient in equation (14) for the solubility. Then

$$R\ln(a_B) = R\ln \gamma_B x_B = -\int_{T_M}^{T} \frac{\Delta H_f}{T^2}\, dT \quad \ldots\ldots\ldots\ldots\ldots (17)$$

where,

γ_B = activity coefficient of the solute in the saturated solution at temperature T

$T << T_M$

When the temperature $T <<$ melting temperature T_M, the variation of ΔH_f with T must be considered first before integrating the equation (14). Generally, ΔH_f is a function of temperature and is given by

$$\Delta H_f = \Delta H_M - \int_T^{T_M} \Delta C_p dT \quad \ldots\ldots (18)$$

where,

ΔH_f = heat of fusion at temperature T,

ΔH_M = heat of fusion at temperature T_M

ΔC_p = difference between the specific heats of liquid and solid,

= (C_p) liquid − (C_p) solid

If the heat capacity of the pure solid and the pure liquid of the salt can be expressed by a relation of the form $C_p = a + bT + c/T^2$, where a, b, c are constants, then $\Delta C_p = \Delta a + T\Delta b + \frac{\Delta c}{T^2}$.

Then from the equation for an equilibrium between a pure solid and a liquid mixture, viz

$$\frac{d\ln(a_B)}{d(1/T)} = -\frac{\Delta H_f}{R} \quad \ldots\ldots (19)$$

and integrating equation (18),

$$\ln(a_B) = \ln \gamma_B x_B$$

$$= -\frac{\Delta H_M}{R}\left[\frac{1}{T} - \frac{1}{T_M}\right] + \Delta a\left[\frac{T_M}{T} - 1 - \ln(T_M/T)\right] +$$

$$\frac{\Delta b}{2}\left[\frac{T_M}{T} - 2T_M + T\right] + \frac{\Delta c}{2R}\left[\frac{1}{T} - \frac{1}{T_M{}^{2}}\right] \ldots\ldots\ldots \quad (20)$$

where γ_B depends on the solute-solvent interactions — as discussed above(27) — at the temperature T.

C. DIFFUSION IN SALT MELTS

Diffusion results from the casual character of the thermal motion of molecules. According to Fick's law

$$J = -DA\frac{dC}{dx} \qquad \text{.......................................(21)}$$

where,

J = quantity of solute that crosses a boundary of cross-section A in unit time

$\frac{dC}{dx}$ = concentration gradient

D = diffusion coefficient

Diffusion in solution can be treated by means of the theory of absolute reaction rates. The process of diffusion is very similar to that of viscous flow in liquids with the exception that in the former case liquid molecules are involved whereas in diffusion in solution a molecule of solute and one of solvent are required to slip past each other. In both, the molecules (or the local structures) pass through a free-energy barrier, the free energy of activation for the molecular transport process. Eyring proved that:

$$DN\frac{dC}{dx} = N\lambda^2 k\frac{dC}{dx} \qquad \text{.................................(22)}$$

Then,

$$D = \lambda^2 k$$

where, λ is the distance between the two successive equilibrium positions,

N = Avogadro number

k = the specific reaction rate for diffusion, i.e. the number of times a molecule moves from one position to the next per second.

This equation holds only for ideal solutions, or dilute solutions that approximate to ideal behaviour. For systems that depart appreciably from ideality, so that the standard free energies are different in initial and activated states, a modified treatment must be given in which case the equation for the resultant flow (M) is given by the following equation:

$$M = NC\lambda D_f - N\left(C + \lambda\frac{dC}{dx}\right)\lambda D_b \quad \ldots\ldots\ldots\ldots\ldots\ldots (23)$$

where D_f and D_b are the specific rates for diffusion in the forward and backward directions. Approximate solutions to this equation have been derived by Eyring(28) and Stern (29).

Experimental work

The self-diffusion of Na^+ ions in molten NaCl has been measured by Bockris(30) by means of radioactive and stable isotopes as tracers. The inter-diffusion coeffients of several metal cations in dilute molten mixtures were measured by Harrison(31) and Höchberg(32), and reviewed by Lorenz(33).

The experimental results were described by an Arrhenius equation

$$D = D_{\infty} e^{-E_D/RT} \qquad (24)$$

More recent inter-diffusion studies by Laity and Miller(34) indicated that values obtained in the earlier work are likely to be too high due to uncontrolled mixing by convection.

II. CRYSTALLISATION WITH CONTINUOUS DEVELOPMENT OF SUPERSATURATION

General

Crystallisation can be carried out in two distinct ways, viz (i) crystallisation from supersaturated solutions at constant temperatures, and (ii) crystallisation with continuous development of supersaturation.

In the first case, the solution is heated to a temperature T_i. Generally, $T_i \ll T_f$, the melting temperature of the solute. The solution at T_i is then rapidly cooled to and kept at the crystallisation temperature (T_o). During cooling from T_i to T_o, seeds are formed at some temperature T_i' slightly below T_i. The excess material then deposits with time onto the seeds formed until the final crystal size is reached.

A survey of literature shows that no work on crystallisation from supersaturated solutions at constant temperature had hitherto been done except that of Roy and Packter.(35)

In the second case, many crystallisations in aqueous solutions and melts are carried out with continuous development of supersaturation by slow mixing, evaporation and cooling of hot saturated solutions. These systems can be schematically represented on a phase diagram as follows:

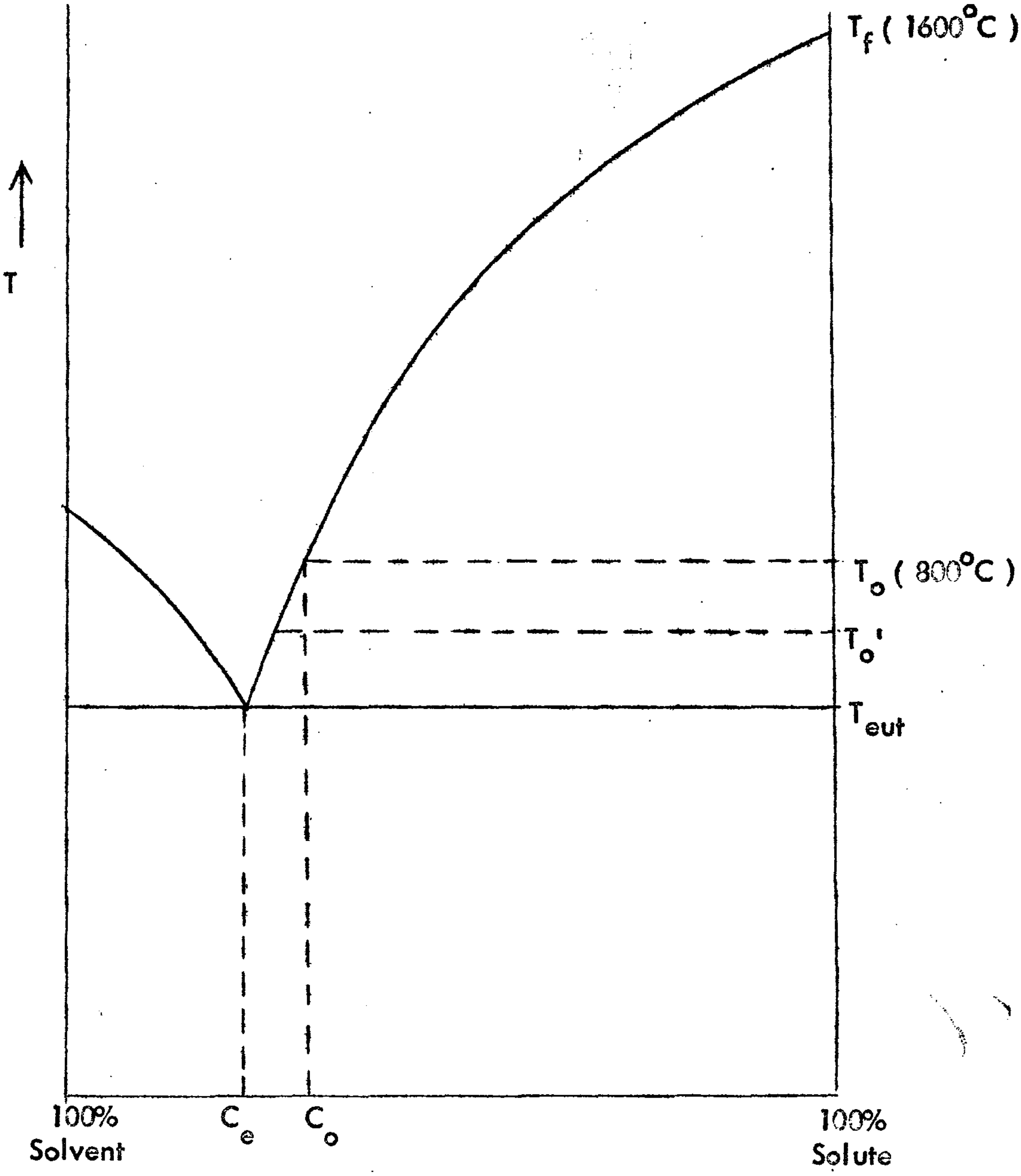


Fig. 1

On the diagram, T_o represents the initial starting temperature and the corresponding saturation concentration of solute (MXO_4) in solvent is C_o. The system is then cooled down to below the eutectic temperature at some constant rate of cooling ($R_T = dT/dt$) that is a constant rate ($R_C = dC/dt$) of development of excess solute concentration, where $R_C = R_T \, . \, dC/dT$. During cooling, nuclei develop from $t = 0$ to $t = \bar{t}$ (if there is any $\bar{t}$), an induction period, that is from $T = T_o$ to $\bar{T}$ (induction temperature). As the temperature decreases at a constant rate, more and more of excess concentration will develop and the excess material will then deposit onto the first nuclei formed to develop bigger crystals. This process will continue until the temperature reaches the eutectic point. Generally, at time t, crystallisation temperature (T_X) equals ($T_o - R_T t$).

A. NUCLEATION

If there is no induction period, excess supersaturation concentration builds up almost immediately after the onset of cooling, then this excess solute concentration gradually increases as the temperature decreases. Generally, in such cases, nucleation and growth process occur simultaneously up to a limit and then only growth process predominates.

Several workers (36-41) have noted that in the case of crystallisation by slow development of supersaturation far longer induction periods may be observed than with rapid mixing. During the induction periods there is only gradual development of excess supersaturation concentration. So rates of nucleation and overall number of nuclei at any time are very low. There is some very slow growth onto these early nuclei. Eventually, after a more prolonged time interval the number and overall surface area become quite large and — as with rapid cooling — the "growth surge" takes place. In some cases, the excess concentration at the induction period is high and growth is then completed within a short time (after this induction period).

B. 'CRITICAL TIME' AND 'CRITICAL TEMPERATURE'

(VARIATION WITH RATE OF DEVELOPMENT OF SUPERSATURATION)

Generally, these induction periods or 'critical times' for crystal growth with slow development of concentration ($\bar{t}_{slow}$) are far greater than induction periods ($\bar{t}_{inst}$) for crystal growth with instantaneous development of solute concentration. Sahay and Packter (41) studied the variation of induction periods for the crystallisation of $BaCrO_4$ with rate of slow mixing. As rate of mixing (R_C = dC/dt) is reduced, $\bar{t}$ increases until at some critical rate, $\bar{t}$ = t_C (the time of mixing). On further reduction of R_C, $\bar{t}$ becomes gradually smaller and smaller than t_C ; at very low rates of mixing $\bar{t}$ may become $\nless 0.01\ t_C$, i.e. $\bar{t} \ll t_C$.

In other words, crystallisation by slow development of solute concentration is similar to a two-stage process, (i) growing of seeds up to the induction period, and (ii) slow growth onto these seeds after the induction period.

Other workers (42-46) studied 'critical temperature' in the slow crystallisation of soluble metal salts from aqueous solutions by slow cooling of saturated solutions at higher temperatures. Generally, $\Delta\bar{T}$ ($\bar{C}$ or $\bar{S}$) increased as rate of cooling (R_T) was decreased. Nyvlt (46) presented some interesting experimental results for the variation of $\Delta\bar{T}_{max}$ (maximum undercooling. The induction period $\bar{t}$ (or $\bar{t}_{max}$) would then be $\Delta\bar{T}_{max}/R_T$.

He showed that :

$$\Delta\bar{T}_{max} = c.R_T^{1/m} \quad \ldots\ldots (25)$$

where m is the nucleation order. That is,

$$\bar{t} = c\,\frac{R_T^{1/m}}{R_T^{\delta}} = \frac{c}{R_T^{\delta}} \quad \ldots\ldots (26)$$

where,

c = constant

$\delta = (1 - 1/m)$.

The m-values varied from <2 to 5. So the δ-values would vary from 0.02 — 0.88.

No quantitative work on this aspect has been reported for crystallisation from melts. An improved theory will be presented in the thesis paper.

Variation of N with $\bar{S}$ ($\bar{C}$)

(46)

For constant R_S (= dS/dt, the rate of development of supersaturation),

$$\frac{dN}{dt} = \frac{J}{R_S} = \frac{k'e^{-B/(\ln S)^2}}{R_S} \quad \ldots\ldots (27)$$

where,

$B = (\beta v_l^3/kT)\,\sigma^3$

v_l = molecular or mean ionic volume

σ = surface energy (solid/liquid) per unit area of solid.

The number ($\bar{N}$) of nuclei developed at supersaturation $\bar{S}$ (at $t = \bar{t}$) is then

$$N = \int_0^{\bar{S}} \frac{k' \exp\left[-B/(\ln S)^2 \right]}{R_S} \, dt \quad \text{.............................. (28)}$$

This equation has not been integrated. At moderate to high supersaturation only,(46)

$$\frac{dN}{dt} = k_n C^p = k_n (R_C t)^p \quad \text{.................................. (29)}$$

$$\therefore N_{\text{at } t = \bar{t}} = \int k_n (R_C t)^p \, dt$$

or,

$$N = k_n R_C^p \frac{(\bar{t})^{p+1}}{p+1} \quad \text{.................................. (30)}$$

Alternatively,

$$\frac{dN}{dC} = \frac{J}{R_C} = \frac{k_n C^p}{R_C}$$

where J = Flux

$$\therefore N_{\text{at } C = \bar{C}} = \int_0^{\bar{C}} \frac{k_n C^p}{R_C} \, dC$$

$$= \frac{k_n (\bar{C})^{p+1}}{R_C (p+1)} \quad \text{.............................. (31)}$$

Generally, in the absence of heterogenous nucleation, $\bar{N}$-values for slow development of supersaturation are much lower than N-values for rapid mixing.