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KINETIC PARAMETERS AND THERMODYNAMIC PROPERTIES OF DIFFUSION-CONTROLLED CRYSTAL GROWTH OF CALCIUM TUNGSTATE FROM SOLUTIONS IN SODIUM TUNGSTATE MELTS BY DIFFERENTIAL THERMAL ANALYSIS

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From DTA curves, energy (E), enthalpy (ΔH_a), entropy (ΔS_a) and free-energy (ΔG_a) of activation and the pre-exponential factor (k_0) for diffusion-controlled crystal growth of calcium tungstate from solutions in sodium tungstate melts were estimated using the Arrhenius equation $k_{DI} = k_0 e^{-E/RT}$. E increased linearly with increased cooling rate (R_T). The change of k_0 was parallel to that of k_{DI} and increased with increasing R_T but there was no direct correlation. ΔH_a, ΔS_a and ΔG_a were unaffected by the changes of R_T and crystallization temperature (T_0). The distance (d_{12}), between a diffusing particle and its host crystal necessary for a successful diffusion, was estimated. Such distances increased with increasing T_0 and R_T.

Over the last decade or so several methods have been developed to study the kinetic analysis of reactions based on DTA curves [1—6] in connection with the determination of the fraction of a substance decomposed during a reaction. Weber and Gottfried [2], Reich [3, 4], Tateno [5] and others have reported different ways of estimating kinetic parameters from DTA curves of various substances using an ordinary Arrhenius equation

$$k = k_0 e^{-E/RT} \tag{1}$$

Hitherto, however, no such studies on the crystallization of alkaline-earth metal salts from solutions in melts have been reported. This paper presents a differential thermal analysis method of estimating the thermodynamic properties, the pre-exponential factor and the distance between a diffusing species and the host crystal for a successful diffusion for diffusion-controlled crystal growth of calcium tungstate from solutions in sodium tungstate melts in platinum crucibles.

Thermodynamics

The rate and therefore the rate constant of a reaction usually increases with temperature, and the dependence of k on T can generally be represented fairly accurately by the empirical Arrhenius equation [1]. Since E and k_0 depend on the rate-controlling process, for a crystal growth process if the correct mechanism

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and the relevant rate-constant are known, Eq. 1 can be applied, and it is then possible to estimate E and k_0 from a plot of $\ln(k) \sim 1/T$. For a diffusion-controlled crystal growth, this equation becomes

$$k_D = k_0 e^{-E/RT} \tag{2}$$

where k_D is the diffusion rate-constant. This equation is of the same form as the Boltzmann equation. Equation 2 may therefore be interpreted by postulating that an atom (or a molecule) must attain an activated state by acquiring an amount of energy E in excess of its normal state before it can diffuse into the surface of a growing crystal. The factor k_0, on the simplest assumption, is equal to the number of diffusion encounter (Z) between a diffusing particle and a growing crystal. For some crystallization processes the values of k_0 are of the expected order 10^{11} but for many others, k_0 is smaller than Z by factors as large as 10^{10}. The discrepancy is dealt with in the collision theory [7, 8] by writing $k_0 = PZ$, where P is a probability factor which may be smaller than unity and which can be interpreted in various ways. Then Eq. 2 may be written,

$$k_D = PZe^{-E/RT} \tag{3}$$

The idea of activation as a pre-requisite is given more precisely in the "transition state theory" [9]. The transition state (X) may be represented as,

$$\text{Reactants} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{X} \xrightarrow{k_3} \text{Product}$$

The ascent of the energy barrier is treated as a thermodynamic equilibrium and is assigned an equilibrium constant K_e defined by k_1/k_2 which is temperature-dependent according to the usual equation

$$RT \log_e (K_e) = \Delta G_a = \Delta H_a - T\Delta S_a \tag{4}$$

where ΔG_a, ΔH_a and ΔS_a are the free-energy, enthalpy and entropy of activation. The overall rate-constant k of a reaction will then be given by $k = K_e k_3$. k_3 can be shown by statistical mechanics to have the universal value RT/Nh, where N is the Avogadro number and h the Planck constant. Hence Eq. 4 becomes,

$$k = (e^{\Delta S_a/R})(RT/Nh)(e^{-\Delta H_a/RT}) \tag{5}$$

and replacing k by k_D,

$$k_D = (e^{\Delta S_a/R})(RT/Nh)(e^{-\Delta H_a/RT}) \tag{6}$$

In this equation, the activation enthalpy ΔH_a is related to the experimental activation energy E by the relation,

$$E = RT + \Delta H_a \tag{7}$$

Comparing Eqs 3 and 6,

$$P \simeq e^{\Delta S_a/R} \tag{8}$$

$$Z \simeq RT/Nh \tag{9}$$

Hence, if k_D and E are known, the values of ΔH_a, ΔS_a, ΔG_a and P may be estimated from Eqs 3 to 9.

When a diffusing particle and a growing crystal approach to within a distance say $r = d_{12}$, it is assumed that the reacting partners stick together, and diffusion occurs. However, the potential energy barrier must be surmounted before diffusion can occur. The height of the potential energy barrier, which is equal to the minimum energy required for diffusion, is taken as the activation energy. From kinetic theory it can be established that,

$$k_D = 2d_{12}^2 (2\pi RT/M^*)\, e^{-E/RT} \tag{10}$$

where $M^* = M_1M_2/(M_1 + M_2)$, M_1 and M_2 being the molecular weights. Therefore, if k_D and E are known, the separation distance (d_{12}) between a diffusing particle and its host crystal can be estimated. Such values are generally of the order of molecular dimensions but higher values may be obtained.

Experimental

The crystallization of calcium tungstate from sodium tungstate melts was carried out at crystallization temperatures $T_0 = 800$ to 1000° at cooling rates $R_T = 0.67$ to 3.3° per minute in a differential thermal analyser (No. 990, E. I. du Pont de Nemours & Co., Wilmington, Del., U.S.A.) as described in an earlier paper [10]. Neglecting the variation of thermal conductivity with temperature the degree of crystallization (α_t) at any crystallization time (t) may be expressed,

$$\alpha_t = A_t/A_{\text{total}}$$

where A_t is the area under ΔT *vs.* t plot at any time t and A_{total} is the total area under the same plot. From the calculated α_t values the length (l_t) of calcium tungstate crystals at any time t was evaluated taking

$$\alpha_t = (l_t/l_f)^3$$

where l_f is the final crystal length.

l_t values were plotted against t and the diffusion rate – constants (k_{D_l}) for growth along the main axis were calculated using the relation

$$k_{D_l} = (\mathrm{d}l/\mathrm{d}t)^2/2aR_T$$

where $a(= \mathrm{d}C/\mathrm{d}T)$ is the rate development of excess solute concentration (C) by cooling. The k_{D_l} values were then plotted against $1/T$ and the gradients determined.

Results

Roy and Appalasami [10] claimed that the growth mechanism of calcium tungstate crystals from solutions in sodium tungstate melts is diffusion controlled; they estimated the diffusion rate-constants for self-diffusion of calcium in calcium tungstate crystals for crystallization by DTA at temperatures T_0 = 800, 900 and 1000°, and cooling rates R_T = 40°, 120° and 200° per hour. In this case, Eq. 2

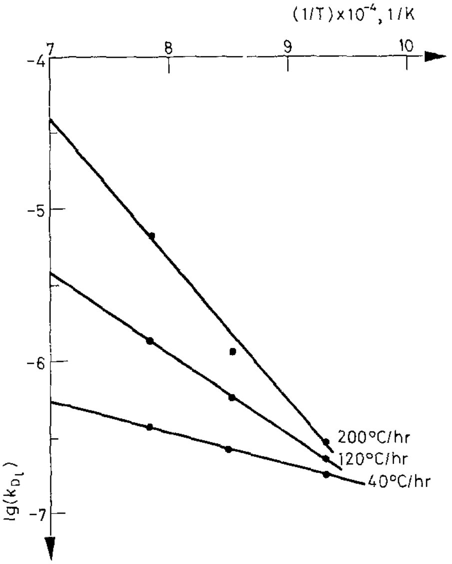

Fig. 1

Table 1

Energy (E), enthalpy (ΔH_a), entropy (ΔS_a) and free-energy (ΔG_a) of activation, pre-exponential factor (k_0), probability factor (P) and the distance for diffusion (d_{12}) for diffusion-controlled crystal growth of calcium tungstate from solutions in sodium tungstate melts

R_T, °C/h	T_0, °C	$10^{-6}k_{D_l}$, cm²/s	$10^{-6}k_0$, cm²/s	$10^{-3}E$, kJ/mol	ΔH_a, kJ/mol	ΔS_a, e.u.	ΔG_a, kJ/mol	P	$10^{-4}d_{12}$, cm
40	800	0.183	0.549	4.276	8.967	0.0377	180.159	1.019	0.685
	900	0.265			9.803		195.770		0.806
	1000	0.364			10.639		211.352		0.926
120	800	0.228	3.758	14.272	8.967	0.0371	179.302	1.018	0.764
	900	0.560			9.799		192.583		1.172
	1000	1.382			10.634		205.187		1.803
200	800	0.291	39.812	22.109	8.963	0.0363	178.349	1.018	0.864
	900	1.147			9.799		189.529		1.677
	1000	6.400			10.634		198.101		3.881

becomes,

$$k_{D_l} = k_0 e^{-E/RT} \tag{11}$$

where k_{D_l} is the average diffusion rate-constant for self-diffusion of calcium into the "wider" growing surface of calcium tungstate crystals. A plot of ln $(k_{D_l}) \sim 1/T$ will be a straight line, and E and k_0 values can then be estimated respectively from the gradient and intercept of this line.

ln $(k_{D_l}) \sim 1/T$ plots (Fig. 1) were drawn using the k_{D_l} values given by Roy and Appalasami [10]. From the estimated E values, ΔH_a, ΔS_a, ΔG_a, P and d_{12} were evaluated (Table 1).

Discussion

Activation energy: The estimated activation energies were rather small, such small values signified that the excess energy over the ground state required by calcium for self-diffusion into the growing calcium tungstate crystals was not high, i.e. not much energy was required to initiate a successful diffusion. E did not increase appreciably with the increase in R_T but maintained a linear relationship, i.e. for a five-fold increase in R_T, E increased almost five times. This indicated that at higher cooling rates, diffusion did not start until higher excess energy (than that for lower cooling rates) was supplied.

The proportionality constant for the direct variation of E with R_T was 0.21×10^{-4} kJh/°C-mol.

When a crystallization process is a combination of several complicated processes, a plot of ln $(k_{D_l}) \sim 1/T$ may not be a straight line. Then it becomes difficult to evaluate E from such a plot. The linearity of the plots in this work indicated that the diffusion-controlled crystal growth of calcium tungstate was not accompanied by other complicated processes.

Activation enthalpy: Since E did not change appreciably with the change in R_T, ΔH_a did not change with R_T either, which was apparent from Eq. 7. The negative ΔH_a indicates that the diffusion process was accompanied by absorption of heat.

Free-energy of activation: ΔG_a increased with the increase in T_0 but was virtually unaffected by the change in R_T.

Activation entropy: Like ΔG_a, ΔS_a was also unaffected by the change in R_T but these values were very low indicating low degrees of randomness. This means that at the effective time of diffusion the particles within the solution had attained somewhat ordered arrangement to make the diffusion process easier. However, $P > 1$ indicates that the diffusion process had no definite steric requirements, i.e. no particular orientations of molecules (or atoms) were needed for a successful diffusion encounter. That the transition state was less rigid than the reactants was apparent from the positive ΔS_a.

Pre-exponential factor: the change of k_0 was parallel to that of k_{D_1} and increased with the increase in R_T but there was no direct correlation.

Separation distance d_{12}: The estimated d_{12} values were rather higher than the order of molecular dimensions. The order of d_{12} depends on the order of the rate-constant. In this work, k_{D_1} was rather high, so also d_{12}. However, the high values of d_{12} are more rightly attributed to the less intimate contact between the diffusing particles and the host crystals than that required for a chemical reaction. The very nature of the reaction in this work was one of self-diffusion of calcium into the growing surfaces of calcium tungstate crystals.

d_{12} increased with the increase in T_0 and R_T, which is consistent with the increase of k_{D_1} with T_0 and R_T. This probably means that the higher the supplied thermal energy the wider was the gap between a diffusing particle and its host crystal surface, and therefore more activation energy was necessary for a successful diffusion.

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Résumé — On a estimé, à partir de courbes ATD, l'énergie *(E)*, l'enthalpie (ΔH_a), l'entropie (ΔS_a) et l'enthalpie libre (ΔG_a) de l'activation ainsi que le facteur pré-exponentiel (k_0) de la croissance des cristaux, contrôlée par la diffusion, du tungstate de calcium, dans des solutions de tungstate de sodium fondu, à l'aide d'une équation d'Arrhenius ordinaire: $k_D = k_0 e^{-E/RT}$. E augmente linéairement avec les vitesses croissantes de refroidissement (R_T), k_0 est parallèle à k_D et augmente quand R_T croît; cependant il n'y a pas de corrélation directe. ΔH_a, ΔS_a et ΔG_a restent indépendants des variations d'R_T et de la température de cristallisation (T_0). On a estimé la distance (d_{12}) nécessaire, entre une particule en diffusion et son cristal-hôte, pour une diffusion réussie. Ces distances augmentent avec les valeurs croissantes de T_0 et R_T.

Zusammenfassung — Aus DTA-Kurven wurden Energie *(E)*, Enthalpie (ΔH_a), Entropie (ΔS_a) und freie Energie (ΔG_a) der Aktivierung, sowie der prä-exponentielle Faktor (k_0) für das diffusionsbedingte Kristallwachstum von Calciumwolframat aus Natriumwolframatschmelzen unter Anwendung einer gewöhnlichen Arrheniusgleichung $k_D = k_0 e^{-E/RT}$ abgeschätzt. Mit zunehmenden Abkühlgeschwindigkeiten *(RT)* nimmt E linear zu. k_0 verhält sich parallel zu k_D und nimmt mit steigendem R_T zu, jedoch ohne direkte Korrelation. ΔH_a, ΔS_a und ΔG_a verhielten sich unabhängig von Änderungen von R_T und der Kristallisationstemperatur (T_0). Die zur erfolgreichen Diffusion erforderliche Entfernung (d_{12}) zwischen einem diffundierenden Teilchen und seinem Empfängerkristall wurde geschätzt. Diese Abstände nahmen mit steigendem T_0 und R_T zu.

Резюме — Используя обычное уравнение Аррениуса $k_{\text{Д}1} = k_0 e^{-\text{E/RT}}$, из кривых ДТА были вычислены энергия активации (E), энтальпия (ΔH_a), энтропия (ΔS_a), свободная энергия (ΔG_a) активация и предэкспоненциальный фактор (k_0) для диффузионно-контролируемого роста кристаллов вольфрамата кальция из расплавов вольфрамата натрия. Энергия активации (E) линейно увеличивается с увеличением скорости охлаждения (R_T). Предэкспоненциальный фактор (k_0) был параллелен $k_{\text{Д}1}$ и увеличивался с увеличением R_T, но прямой корреляции не было замечено. Значения ΔH_a, ΔS_a, ΔG_a не затрагивались ни изменением R_T, ни температурой кристаллизации (T_0). Было оценено расстояние (d_{12}) между диффузионной частицей и кристаллом «хозяином», что необходимо для успешной диффузии. Эти расстояния увеличиваются с увеличением T_0 и R_T.