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Studies of the Estimation of the Interfacial Energy of Embryo in Solid-Liquid Systems

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A novel method for the estimation of the interfacial energy of an embryo from the solubility data in solid-liquid systems has been proposed. The distribution function of embryos in solutions derived thermodynamically has been used as the base for the present treatment. The interfacial energies were calculated numerically for three different combinations of solute and solvent, namely, water-inorganic salt, water-organic compound, and organic solvent-organic compound. A fairly good linear relationship was observed between the interfacial energies calculated and the temperatures over the whole temperature range of solubility data. The semiempirical equation describing the relationship between the interfacial energy of the embryo and the temperature in the solid-liquid system was found to be exactly the same as that between the surface energy of the liquid in contact with gas through a free surface and the temperature. The size dependence of the interfacial energy has also been briefly described.

With regard to the nucleation phenomena in both gas and liquid phases, it has been concluded theoretically that the interfacial energy is an important physical property directly affecting the nucleation rate. In spite of the importance of the interfacial energy of embryo in solid liquid systems, however, few reports have been published so far. Accordingly, the determination of the interfacial energy of the embryo seems to be indispensable to developing the nucleation study in solid-liquid systems.

The interfacial energies of the embryo in solid-liquid systems have been sporadically determined from the measurements of the excess solubility of finely-divided crystals,$^{1-4)}$ the waiting time in the critical nucleus formation,$^{5-7)}$ and the nucleation rate.$^{8-10)}$ Because of many theoretical and experimantal difficulties, the numerical values of the interfacial energy reported so far differ from one another depending on the method of measurement and the investigator, and the values are considered to be unreliable. Moreover, the temperature dependence of the interfacial energy in solid-liquid systems has not been studied at all. In this paper, a method of estimating the interfacial energy of the embryo from the solubility data is proposed, and its numerical values over the entire temperature ranges of the solubility data are calculated for a large number of solid-liquid systems. In addition, both the temperature- and the size-dependences of the interfacial energy are described.

Theoretical

It is generally recognized that a great number of embryos of various sizes are present in a supersaturated solution.[*1] According to this concept, it is possible to derive a distribution function of the embryos in a supersaturated solution.

Let X_{nj} be the number fraction of embryos composed of j molecules of solute, and assume that the interfacial energy is independent of both the embryo size and the solution composition. For an ideal solution, the change in the Gibbs free energy due to the coagulation of j molecules is given by:$^{11,12)}$

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1) G. A. Hulett, *Z. Phys. Chem.*, **37**, 385 (1901); **47**, 357 (1904).

2) A. R. Tourky and S. E. S. El Wakkad, *J. Phys. and Coll. Chem.*, **53**, 1126 (1949).

3) Van Zeggeren and G. C. Benson, *Can. J. Chem.*, **35**, 1150 (1957).

4) B. V. Enüstün and J. Turkevich, *J. Am. Chem. Soc.*, **82**, 4502 (1960).

5) G. Preckshot and G. G. Brown, *Ind. Eng. Chem.*, **44**, 1314 (1952).

6) A. C. Chatterji and R. N. Singh, *J. Phys. Chem.*, **62**, 1408 (1958).

7) R. Gindt and R. Kern, *Compt. Rend.*, **562**, 4186, 4400 (1963).

8) J. C. Fisher, J. H. Holloman and D. Turnbull, *Science*, **109**, 168 (1949).

9) H. Naono and M. Miura, This Bulletin, **38**, 80 (1965).

10) H. Naono, *ibid.*, **40**, 1104 (1967).

[*1] An embryo is defined as a molecular aggregate the aggregation number of which ranges from two to a number less than that in a critical nucleus.

11) H. Reiss, *Ind. Eng. Chem.*, **44**, 1284 (1952).

12) A. E. Nielsen, "Kinetics of Precipitation," Pergamon Press, Oxford, London (1964), p. 7.

$$\Delta g = -j\phi + \beta\sigma j^{2/3} + \boldsymbol{k}T \ln Xn_j \qquad (1)^{*2}$$

where Δg is the Gibbs free energy change per j molecules; ϕ, the Gibbs free-energy change per molecule; β, the geometric factor of the embryo; $\boldsymbol{\sigma}$, the interfacial energy; $\boldsymbol{k}$, the Boltzmann constant, and T, the absolute temperature. The number fraction of embryos composed of j molecules of the solute, X_{nj}, is defined by:

$$Xn_j = \frac{n_j}{\sum_{j=2}^{j} n_j + n_1 + n_s} \qquad (2)$$

where n_j is the number of embryos composed of j molecules of the solute; $\sum_{j=2}^{j} n_j$, the number of embryos of various sizes; n_1 the number of monomolecules of the solute, and n_s, the number of solvent molecules.

When the equilibrium of the embryo distribution in a supersaturated solution is accomplished, Δg becomes zero and Eq. (1) reduces to:

$$Xn_j = \frac{n_j}{\sum_{j=2}^{j} n_j + n_1 + n_s} = \exp\left(-\frac{\beta\sigma j^{2/3} - j\phi}{\boldsymbol{k}T}\right) \qquad (3)$$

and

$$n_j = \left(\sum_{j=2}^{j} n_j + n_1 + n_s\right) \exp\left(-\frac{\beta\sigma j^{2/3} - j\phi}{\boldsymbol{k}T}\right) \qquad (4)$$

If it is possible to extend this distrubition function to the saturated state, ϕ should become zero; Eq. (4) can then be rewritten as:

$$n_j = \left(\sum_{j=2}^{\infty} n_j + n_1 + n_s\right) \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right) \qquad (5)$$

where the upper limit of the summation is taken to infinity, since the number of solute molecules in the critical nucleus is considered to be infinite in a saturated solution.

If the number of the monomolecules of the solute is also assumed to be expressed by Eq. (5), the total number of embryos of various sizes and monomolecules is given by:

$$\sum_{j=2}^{\infty} n_j + n_1 = \sum_{j=1}^{\infty} n_j = \left(\sum_{j=1}^{\infty} n_j + n_s\right)\left\{\sum_{j=1}^{\infty} \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)\right\} \qquad (6)$$

Accordingly, the number of solvent molecules is given by:

$$\begin{aligned} n_s &= \left(\sum_{j=1}^{\infty} n_j + n_s\right) - \sum_{j=1}^{\infty} n_j \\ &= \left(\sum_{j=1}^{\infty} n_j + n_s\right)\left\{1 - \sum_{j=1}^{\infty} \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)\right\} \end{aligned} \qquad (7)$$

When all the embryos of various sizes dissociate to monomolecular solutes, the total number of monomolecular solutes is given by:

$$\sum_{j=1}^{\infty} jn_j = \left(\sum_{j=1}^{\infty} n_j + n_s\right)\left\{\sum_{j=1}^{\infty} j \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)\right\} \qquad (8)$$

Finally, the so-called "*solubility*" in the mole fraction can be expressed as follows:[*3]

$$solubility = \frac{\sum_{j=1}^{\infty} jn_j}{\sum_{j=1}^{\infty} j\cdot n_j + n_s} = \frac{\sum_{j=1}^{\infty} j \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)}{\sum_{j=1}^{\infty} j \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right) + 1 - \sum_{j=1}^{\infty} \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)} \qquad (9)$$

The average number of solute molecules per embryo in a saturated solution, j_{av}, may be estimated in the following manner:

$$j_{av} = \frac{\sum_{j=2}^{\infty} jn_j}{\sum_{j=2}^{\infty} n_j} = \frac{\sum_{j=2}^{\infty} j \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)}{\sum_{j=2}^{\infty} \exp\left(-\frac{\beta\sigma j^{2/3}}{\boldsymbol{k}T}\right)} \qquad (10)$$

where the lower limit of the summation is taken as two, since the aggregate composed of two or more molecules is defined as an embryo.

The dimensionless quantity included in the above equations is then replaced by:

$$\frac{\beta\sigma}{\boldsymbol{k}T} \equiv K \qquad (11)$$

By substituting Eq. (11) into Eqs. (9) and (10), one obtains:

$$solubility = \frac{\sum_{j=1}^{\infty} j \exp(-Kj^{2/3})}{\sum_{j=1}^{\infty} j \exp(-Kj^{2/3}) + 1 - \sum_{j=1}^{\infty} \exp(-Kj^{2/3})} \qquad (12)$$

$$j_{av} = \frac{\sum_{j=1}^{\infty} j \exp(-Kj^{2/3})}{\sum_{j=2}^{\infty} \exp(-Kj^{2/3})} \qquad (13)$$

The relationship between the *solubility* or j_{av} and the K value can be determined by the numerical calculation using Eqs. (12) and (13), since the *solubility* and j_{av} are the functions of only K. If the embryo is assumed to be a sphere, β should be expressed as:

$$\beta = (4\pi)^{1/3}(3v)^{2/3} \qquad (14)$$

[*2] The present author is aware that the use of the term "interfacial energy" is not always appropriate, since the idea of an "interface" between a solution and an embryo composed of only a few solute molecules is purely formal. In such a case the term should simply be understood as a word meaning the excess energy which is inherent in the embryo formation.

[*3] The solubility in the mole fraction is usually defined as the ratio of the number of monomolecular solutes to the number of both monomolecular solutes and solvents. In the present paper, however, the number fraction defined by Eq. (2) is used as the concentration. In order to avoid confusion, italic type is used for the former quantity.

where v is the molecular volume of the solute.

The results of the numerical calculation for the *solubility* and j_{av} as a function of K are shown in Figs. 1 and 2 respectively.

The interfacial energy and the average number of solute molecules per embryo in a saturated solution can be obtained through the following procedures: 1) the calculation of the *solubility* at an arbitrary temperature from the solubility data; 2) the determination of K corresponding to the *solubility* from Fig. 1; 3) the calculation of β by Eq. (14); 4) the calculation of σ corresponding to the K obtained by means of Eq. (11), and 5) the determination of j_{av} corresponding to K from Fig. 2.

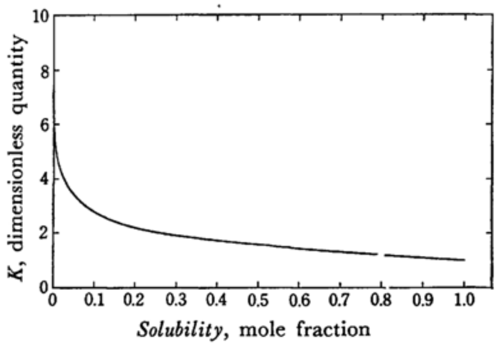

Fig. 1. Relationship between K and *solubilty*.

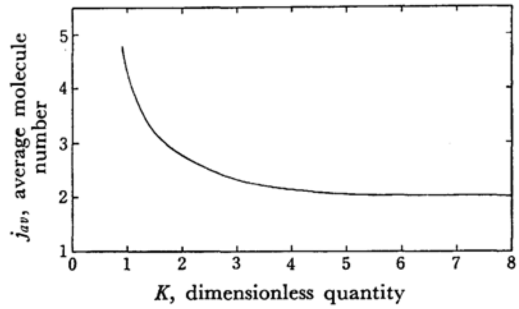

Fig. 2. Relationship between j_{av} and K.

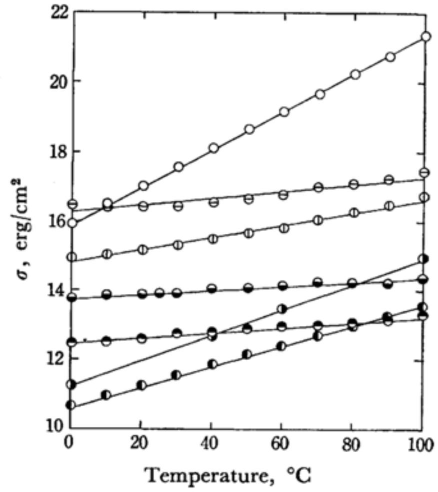

Fig. 3. Relationship between σ and the temperature for easily-soluble anhydrous salts in water.
○: NaCl ⊖: K_2SO_4 ⦶: KCl ◑: ZnI_2
◒: NH_4Cl ◐: K_2CrO_4 ◓: NH_4Br

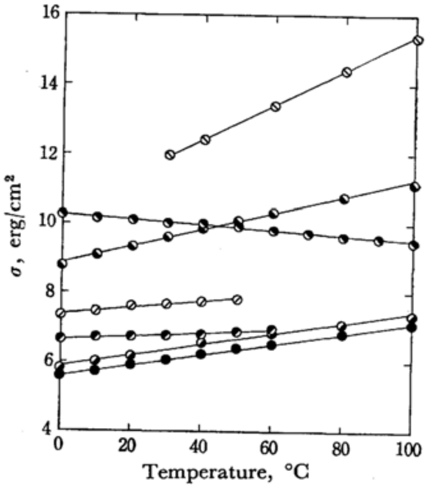

Fig. 4. Relationship between σ and the temperature for easily-soluble hydrous salts in water.
⦸: $Na_2CO_3 \cdot H_2O$ ◔: $CuSO_4 \cdot 5H_2O$
◐: $LiOH \cdot H_2O$ ⊘: $NaI \cdot 2H_2O$
◐: $SrCl_2 \cdot 6H_2O$ ◑: $MgCl_2 \cdot 6H_2O$
●: $MgBr_2 \cdot 6H_2O$

Results

The present calculation was applied to the solid-liquid systems for which the solubility data were known over a wide temperature range. The systems were selected from "Kagaku Binran."[13] Since Eqs. (12) and (13) should hold for any combination of solute and solvent, the calculation was carried out for three different systems: 1) fifty inorganic salts in water, 2) fifteen organic compounds in water, and 3) fifteen organic compounds in organic solvents.

The interfacial energies for three sorts of inorganic salts, *i. e.*, easily-soluble anhydrides, easily-soluble hydrates, and sparingly-soluble anhydrates, were calculated. Some of the results are shown in Figs. 3, 4 and 5, where the interfacial energy is plotted against the centigrade temperature. As these figures show, a fairly good linearity in the plot of σ values against the centigrade temperatures was obtained for all fifty systems calculated.

Similar calculations were also carried out for both water-organic compound and organic solvent-organic compound systems. Some of the results are shown in Figs. 6 and 7. In these instances linearity was also obtained for all thirty systems.

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[13] "Kagaku Binran," Maruzen, Tokyo (1958), p. 581.

Discussion

Temperature Dependence. The temperature dependence of the surface energy in the gas-liquid system has been studied theoretically by several authors[14,15] and a linear relationship has been concluded to hold. The temperature dependence of the surface energy of liquids which come in contact with gases through a free surface has been experimentally ascertained, and the following empirical equation has been proposed;[16,17]

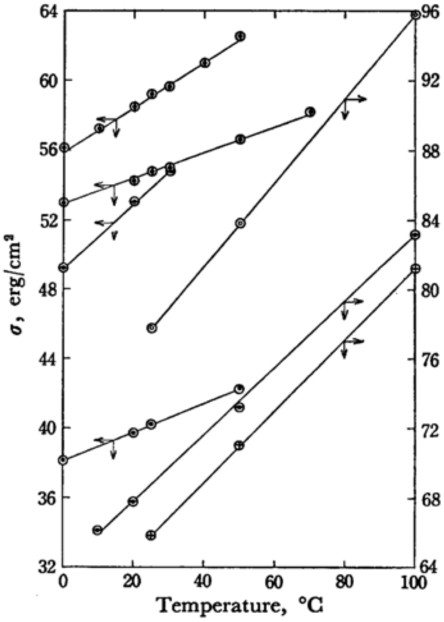

Fig. 5. Relationship between σ and the temperature for sparlingly-soluble anhydrous salt in water.

◍: $PbSO_4$ ⦶: Ag_2CrO_4 ⊖: $SrSO_4$
◎: $CaCO_3$ (Aragonite) ⊙: $BaSiF_6$ ⊜: $BaSO_4$
⊕: $CaCO_3$ (Calcite)

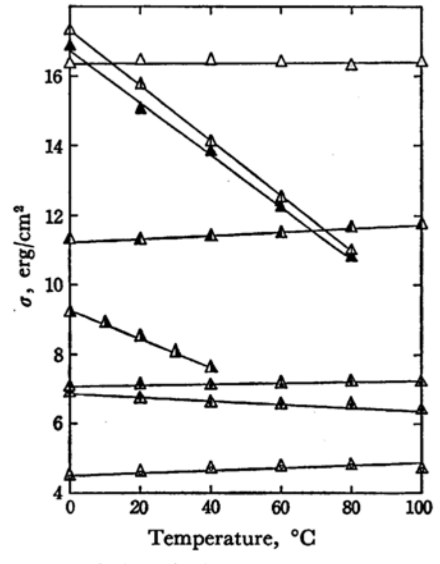

Fig. 6. Relationship between σ and the temperature for organic compounds in water.

△: Picric acid	◬: Succinic acid
▲: Oxalic acid	◮: Potassium oxalate
◭: Cyanamide	⟁: Racemic acid
⟁: Glycine	◬: Sucrose

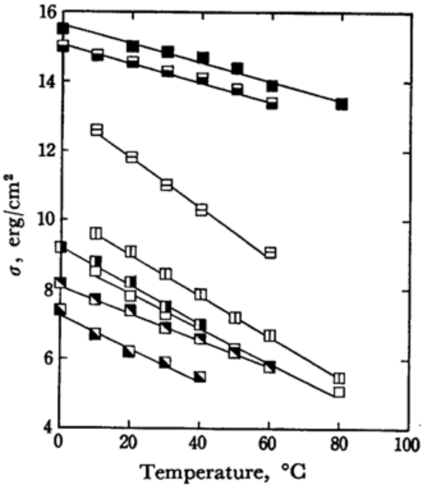

Fig. 7. Relationship between σ and the temperature for organic compound - organic solvent systems.

■: Anthraquinone-benzene
⬓: Anthracene-benzene
⊟: Picric acid - benzene
◫: Benzoic acid - benzene
◨: Acetamide-ethanol
□: Naphthalene-benzene
◪: Acetanilide-ethanol
◩: Urethan-ethanol

$$\sigma\left(\frac{M}{\rho_l}\right)^{2/3} = \alpha(T_c - T - 6) \qquad (15)$$

where M is the molecular weight; ρ_l, the density of the liquid; α, a constant; T_c, the critical absolute temperature of the liquid, and T, the absolute temperature corresponding to σ,

On the other hand, a linear relationship between the interfacial energy of embryo and the temperature was also obtained from the present study for solid-liquid systems. Since v in Eq. (14) is expressed by:

$$v = \frac{M}{\boldsymbol{N}\rho_s} \qquad (16)$$

one obtains, by substituting Eq. (16) into Eq. (14):

$$\beta = (4\pi)^{1/3}\left(\frac{3}{\boldsymbol{N}}\right)^{2/3}\left(\frac{M}{\rho_s}\right)^{2/3} \qquad (17)$$

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14) J. O. Hirschfelder, C. F. Curtiss and B. R. Bird, "Molecular Theory of Gases and Liquids," John Wiley, New York (1954), p. 342.

15) J. Frenkel, "Kinetic Theory of Liquids," Dover Publications, New York (1955), p. 310.

16) R. Eötvös, *Wied. Ann.*, **27**, 456 (1886).

17) W. Ramsay and J. Shields, *J. Chem. Soc.*, **1893**, 1089.

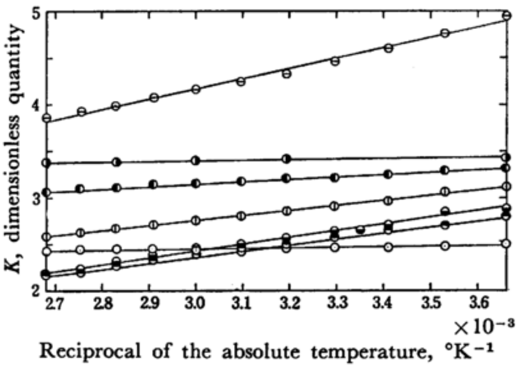

Fig. 8. Relationship between K and the reciprocal of the absolute temperature for easily-soluble anhydrous salts in water.
⊖: K_2SO_4 ◑: ZnI_2 ◐: K_2CrO_4 ⦶: KCl
◒: NH_4Cl ◓: NH_4Br ○: NaCl

where ρ_s is the density of the solute at the solid state and N, the Avogadro number.

The K values lie on a straight line in the plot against the reciprocal of the absolute temperature, as is shown in Fig. 8, in which the same systems as those in Fig. 3 are selected. Therefore, the relationship between K and the absolute temperature is given as:

$$K = A + \frac{B}{T} \tag{18}$$

where both A and B are constants characteristic of their solid-liquid systems.

By substituting Eqs. (17) and (18) into Eq. (11), one can derive the following semi-empirical equation for solid-liquid systems;

$$\sigma\left(\frac{M}{\rho_s}\right)^{2/3} = \frac{Ak}{(4\pi)^{1/3}\left(\dfrac{3}{N}\right)^{2/3}}\left(T + \frac{B}{A}\right) \tag{19}$$

By comparing Eq. (15) with Eq. (19), one can conclude that the temperature dependence of the interfacial energy can be expressed by similar equations for both cases, *i. e.,* liquids coming into contact with gases through a free surface and solid embryos in saturated solutions.

Size Dependence. The size dependence of the surface energy of a small droplet in a gas-liquid system has been thermodynamically studied by Tolman,[18] and the following theoretical equation has been derived:

$$\frac{\sigma_r}{\sigma_\infty} = \frac{1}{1 + \dfrac{2\delta}{r}} \tag{20}$$

where σ_r is the surface energy of the droplet with the radius r; σ_∞, that of the liquid with a free surface, and δ, a constant. Although he suggested that δ should be of the same order as the molecular diameter of liquid species, he did not make any numerical examination, presumably because of the lack of the surface energy data on small droplets in gas-liquid systems.

Since the *solubilities* don't change greatly with the temperature in the systems calculated in the present study, the variation in j_{av} was not appreciable over the whole temperature range. For instance, when the *solubility* of potassium chloride varies from 0.0694 to 0.120, corresponding to the temperature elevation from 0°C to 100°C, the K value changes from 3.06 to 2.50. Accordingly, the J_{av} value obtained from Fig. 2 varies from 2.32 to 2.44 corresponding to the variation of K. Since the variations in j_{av} were unappreciable for all solid-liquid systems studied, it may be reasonable to say that the size effect of the interfacial energy of embryo does not appear in the σ values calculated by the present method.

Comparison with the Published Data. Although the interfacial energies of the finely-divided crystals in solid-liquid systems have been investigated by several authors[1-4,19] on the basis of measuring the excess solubility, the results seem questionable. This is an indication of the number of theoretical and experimental difficulties unavoidable in treating fine particles, as was pointed out by Harbury.[19] The interfacial energies calculated by the present method will be compared below with recently-published data.

Recently, the interfacial energy of strontium sulfate has been estimated by Enüstün and Turkevich[4] utilizing the dependence of the solubility on the particle size. They have given 84±8 erg/cm² as the interfacial energy of the finely-divided crystals (radius, 9 Å) at 25°C. On the other hand, by means of the present method σ and j_{av} are determined to be 53.9 erg/cm² and 2.0 respectively in the saturated solution at 25°C. Assuming that the difference in σ values depends only on the difference in the number of molecules in the two embryos, one can determine δ in Eq. (20). If the embryo is spherical, the radius of the embryo composed of two molecules becomes 3.33 Å. By substituting the σ and r of both embryos into Eq. (20) and by then dividing the former by the latter, one can obtain;

$$\frac{84}{53.9} = \frac{1 + \dfrac{2\delta}{3.33}}{1 + \dfrac{2\delta}{9}} \tag{21}$$

From Eq. (21) δ is calculated to be 2.20 Å. As a result of the above examination, δ seems to be roughly equated to the molecular radius (2.64 Å) of strontium sulfate, where the molecular radius is calculated on the assumption of a spherical molecule.

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[18] R. C. Tolman, *J. Chem. Phys.*, **16**, 758 (1948). **17**, 333 (1949).

[19] L. Harbury, *J. Phys. Chem.*, **50**, 190 (1946).

Van Zeggeren and Benson³⁾ have investigated, by means of the electric-conductivity method, the solubilities of sodium chloride specimens varying in specific surface in ethanol at 25°C. They have given 171 erg/cm^2 as the interfacial energy of the fine crystal with a radius of 325 Å. In the present study the value is 50.9 erg/cm^2 for the embryo with a radius of 2.78 Å. In this system the δ in Eq. (20) becomes 3.37 Å (molecular radius: 2.20 Å)

Fisher *et al.*⁸⁾ have shown that the interfacial energy for the critical nucleus in a water-sucrose system is about 6 erg/cm^2. In the present study the value is 4.6 erg/cm^2 for the sucrose embryo composed of solute molecules of 2.4 at 25°C.

As a whole, the present calculation of the interfacial energies gives somewhat smaller values than those previously reported. This is probably due to the fact that smaller values of the embryo size were here calculated. Since our knowledge of the size dependence of the interfacial energy is insufficient at the present stage, it is difficult to predict in detail the interfacial energies of the fine crystals of various sizes in solid-liquid systems.

The conclusions are that it is possible to estimate the interfacial energy of embryos from the solubility data for all solid-liquid systems and that the interfacial energies calculated are linear in the plot against the temperature, as has been ascertained in gas-liquid systems with a free surface.

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