

The Freezing of Supercooled Droplets of Electrolytic Solutions

R. G. DE PEÑA, J. V. IRIBARNE AND E. M. DE ACHÁVAL

*Instituto de Física de la Atmósfera and Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires and Servicio Meteorológico Nacional, Argentina*

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ABSTRACT

The freezing characteristics of supercooled droplets of electrolytic solutions were studied for a set of 22 electrolytes and for concentrations of 10^{-3} , 10^{-2} and 10^{-1} N. Ethyl alcohol was also tested. The freezing curves were found to be similar to those of water. The mean freezing temperature was compared in each case with that of the water sample used as a solvent. The differences were interpreted for the more diluted solutions in terms of the theory of heterogeneous nucleation.

1. Introduction

Although many authors have studied experimentally the freezing temperature of water droplets (see Mason, 1957), little attention has been given to the study of the freezing properties of droplets of electrolytic diluted solutions.

Lafargue (1950) found that droplets of 1- to $10\text{-}\mu$ diameter of concentrated solutions of NaCl, KI, MgCl_2 and ZnCl_2 , had the same freezing temperature as the water droplets ($-40.5 \pm 1.5\text{C}$).

Bigg (1953a; see also Mason, 1953) determined the freezing temperature of droplets of 0.1- to 5-mm diameter of different electrolytic solutions, using the same technique applied to water droplets (Bigg, 1953a, 1953b). His results may be summarized as follows:

(a) For solutions of NaCl, $(\text{NH}_4)_2\text{SO}_4$, HNO_3 and HI the mean freezing temperature is related to the volume of the droplet by a relation similar to that for pure water (see below, Eq 1), although with different constants.

(b) At moderate concentrations (molar fraction about 10^{-2} or less) NaCl has practically no effect, and the other three electrolytes raise the mean freezing temperature, this effect passing through a maximum; at higher concentrations (approaching a molar fraction 10^{-1}) all of them depress the freezing temperature. The constants of the relation between volume and freezing temperature also vary with the concentration.

(c) He studied a number of electrolytes (halides, nitrates and sulfates of H, Li, Na, K, Cs and NH_4) at a molar fraction of 10^{-3} and found increases of the freezing temperature varying from 0 to 12C ; the data show no simple relation between the effect and the nature of the electrolytes. The ions I^- , F^- , H^+ and Li^+ seem to be more active than others; NH_4I is particularly active.

Hosler and Hosler (1955) and Hosler and Spalding (1955) studied the freezing of droplets of solutions with different techniques. They found that in capillaries the variation of the freezing temperature was a function of the capillary diameter and of the concentration; with droplets deposited on a solid surface, the results were approximately proportional to those capillaries with regard to concentration, except for sizes smaller than $13\text{-}\mu$ diameter, for which the effect was not significant, perhaps due to the evaporation of water from the droplets. These authors tried also some of the soluble chemicals by introducing a spray in a cloud chamber.

All the experiments show clearly that in all cases in which sufficiently high concentrations could be attained, there is a lowering of the mean freezing temperature, which becomes very pronounced as the concentration increases. For small concentrations some of the electrolytes raise the mean freezing temperature up to a maximum located at variable concentrations for the different electrolytes.

Besides these investigations, some authors have made measurements with supercooled clouds in cold chambers. We shall not discuss their results here, as the technique is very different and the data seem to indicate that other factors influence the results (Bigg, 1953a).

In this research we have tried to study in a systematic way the influence of a set of mono-monovalent electrolytes as a function of the concentration, and to derive conclusions about the effect of the individual ions.

2. Technique and Apparatus

Fig. 1 shows a schematic drawing of the experimental device. About 100 droplets of uniform size (± 10 per cent) were deposited upon a highly polished stainless

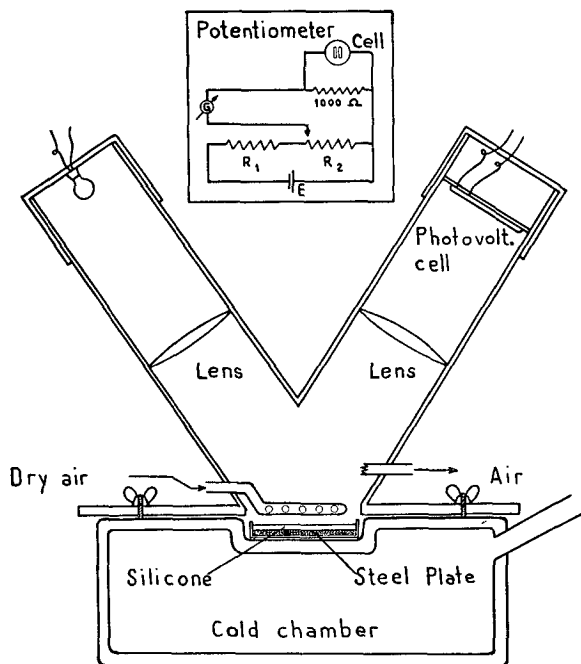


FIG. 1. Apparatus.

steel plate and covered with high viscosity silicone. A light source and a lens insured homogeneous illumination of the plate. The reflected light fell upon a photovoltaic cell whose response was measured with a potentiometer. The plate was placed upon a metallic box which was filled with alcohol and had an opening on one side for introducing dry ice. The system lens-plate-cell was contained in an enclosure with black walls through which dry air was flowed to avoid the tarnishing of the silicone surface by water vapor.

At the beginning of the experiment, the cell current was compensated through the potentiometer. As the cooling proceeded, at the rate α of *ca.* 0.5C per min, the droplets froze and the intensity of the reflected light that reached the cell changed. The consequent variation of the current was measured in the galvanometer simultaneously with the temperature of the plate. The current, which measured the number of frozen droplets, was plotted as a function of the temperature. Fig. 2 shows a typical experiment and the corresponding frequency curve. Similar results were obtained when the frozen droplets were counted directly by looking through a window.

It may be seen that the frequency curve is somewhat asymmetrical. This feature was observed in most experiments and agrees with the results of previous workers. The temperature corresponding to 50 per cent of the droplets frozen was taken as the mean freezing temperature T_{fr} , and the mean supercooling is defined as $\tau = 273.2 - T_{fr}$.

Previous measurements in which the plate material

and the liquid were changed verified that this had no influence on the mean freezing temperature. The following materials were tested: steel, aluminum, polyethylene, steel covered with silicone baked at 300C until dry, paraffin and mercury; the droplets were covered with silicone, toluene and ligroin. In every case the mean freezing temperatures determined for the same sample of water were found to coincide within 0.5C, which is within the limits of error of the method.

3. Results

Pure water. The water was purified by conventional bi-distillation, the second time from a solution of alkaline permanganate. Its conductivity was that of equilibrium water (*ca.* 2×10^{-6} ohm $^{-1}$ cm $^{-1}$). The mean freezing temperature for 1 mm 3 droplets varied between -17 and -27C (mostly between -20 and -25C) for different samples. The exponential law

$$V \cdot e^{\kappa \tau} = a \quad (1)$$

where V is the droplet's volume and κ and a are constants, was verified for diameters between 0.7 and 1.4 mm.

The values of κ and a depended on the water sample. They could be determined from a plot of the left side of Bigg's statistical relation

$$\ln[-\ln(1-P)] = \ln \frac{V \cdot a}{\alpha \cdot \kappa} + \kappa T_s \quad (2)$$

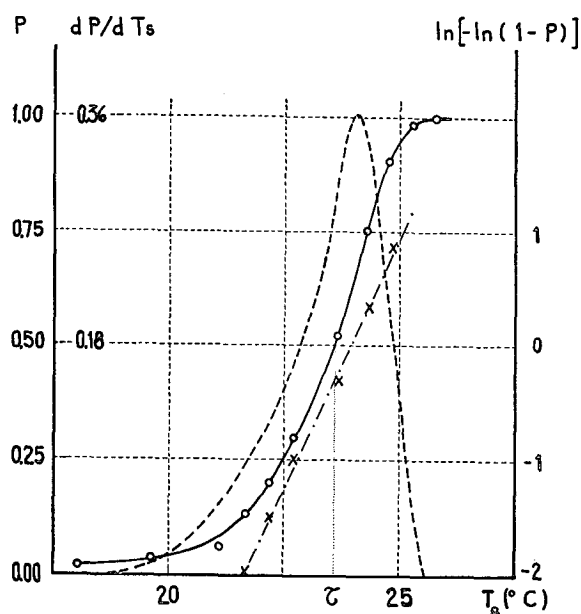


FIG. 2. Typical example of freezing curve. Full line: P , the cumulative distribution of freezing temperatures for 100 droplets. Dashed line: frequency curve dP/dT_s . Straight line: $\ln[-\ln(1-P)]$ (Eq 2).

as a function of the supercooling $T_s = 273.2 - T$ (T being the absolute temperature; see Fig. 2). Here P is the fraction of droplets frozen at T_s , and for $P = 0.5$, $T_s = \tau$. The points fitted fairly well with the formula, although in some cases they showed a definite curvature. To make comparable the results of different experiments, relation (1) was used to refer the results to a droplet size of 1 mm^3 .

Solutions. Different electrolytes were studied at the concentrations 10^{-3} , 10^{-2} , 10^{-1} N. Ethyl alcohol was also tested. The validity of relation (1) was verified for KBr (small effect) and KI at 10^{-1} N (large effect) for droplet diameters between 0.5 and 2.6 mm. The assumption was made that this validity may be extended to all electrolytes tested, so that the results were corrected to a droplet size of 1 mm^3 in a similar way as for pure water. The actual volume of droplets was always close to this value within a factor of 5. The results were also fairly consistent in most cases with relation (2) and the values for a and κ could be derived as in the case of pure water.

Values of κ . Table 1 summarizes the values of the

TABLE 1. Values of κ (formula 1) for water and for solutions of different concentrations.

Type of sample	Number of experiments	κ Average	σ	σ_{av}
Water	58	0.83	0.23	0.03
Solution 10^{-3} N	48	0.86	0.21	0.03
Solution 10^{-2} N	39	0.77	0.25	0.04
Solution 10^{-1} N	34	0.66	0.19	0.03

σ = mean error of single observation.
 σ_{av} = mean error of result.

coefficient κ obtained for pure water and for the various concentrations. In each case the values of all experiments were averaged, irrespective of the particular sample of water or solution examined. A few values (7 in all) were eliminated from the statistics through the Pierce-Chauvenet criterion.

The average values for water and for solutions 10^{-3} and 10^{-2} N show no significant difference. The smaller value for solutions 10^{-1} N seems to indicate an effect of the solutes. There was clearly no correlation between κ and τ in any set of values. Nor was any specific effect apparent from our data for any particular electrolyte, but this may have been because the dispersion of the results was large and the number of experiments for each solution was small. The value of $\kappa_{average}$ for pure water is very close to the value 0.82 found by Bigg for his samples of water.

Mean freezing temperature. For each sample of solution, the mean freezing temperature τ' (where the

prime indicates that the symbol refers to a solution) was compared with the value of τ for the sample of pure water used as a solvent (all values reduced to a droplet size of 1 mm^3), and $\Delta T = \tau - \tau' = T_{fr}' - T_{fr}$ was determined.

As an example, Fig. 3 represents ΔT and τ' as a function of τ for KI solutions prepared with different samples of water. It can be seen that ΔT , and not τ' , should be considered as independent of τ . The dispersion of data for each concentration is typical of the results for most electrolytes.

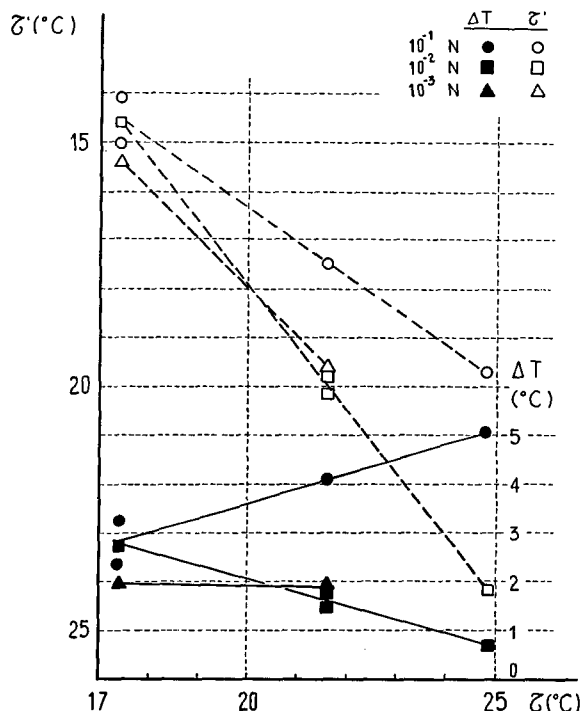


FIG. 3. Influence of the water sample.

The results are summarized in Figs. 4 to 7, where each point gives the average value obtained, and the number of experiments is recorded at its side. For the sake of convenience, the electrolytes have been grouped according to three general types of behavior within the range of concentrations studied:

- (i) $\Delta T > 0$, increasing with the concentration (Fig. 4).
- (ii) $\Delta T > 0$, first increasing with the concentration, and then passing through a maximum or attaining a constant value (Fig. 5).
- (iii) ΔT remains small positive, null or negative throughout the range of concentrations (Figs. 6 and 7).

Ethyl alcohol had no effect at any concentration between 10^{-2} and 1 molar, and this result held true when the drops were covered with different mineral

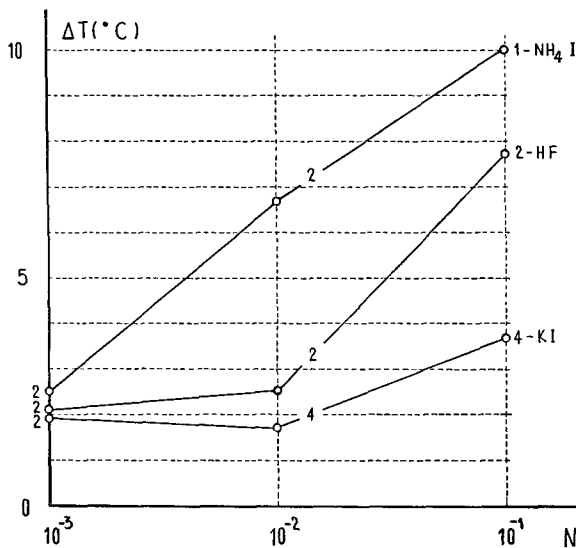


FIG. 4. Influence of the concentration for different electrolytes.

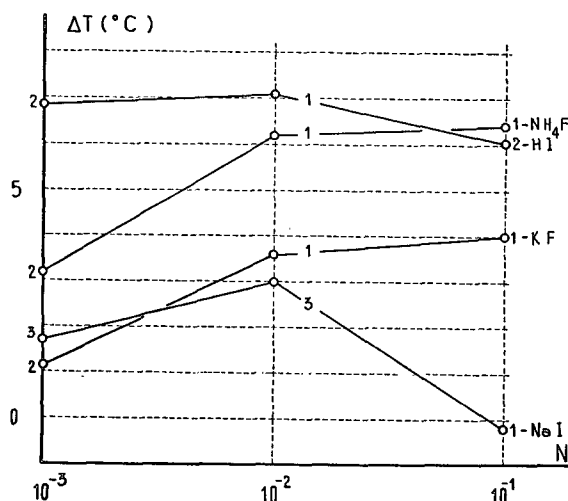


FIG. 5. Influence of the concentration for different electrolytes.

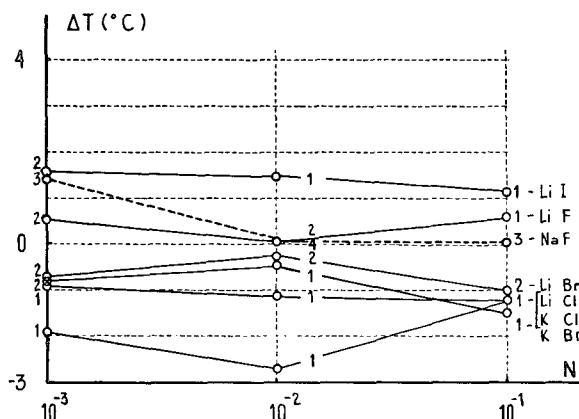


FIG. 6. Influence of the concentration for different electrolytes.

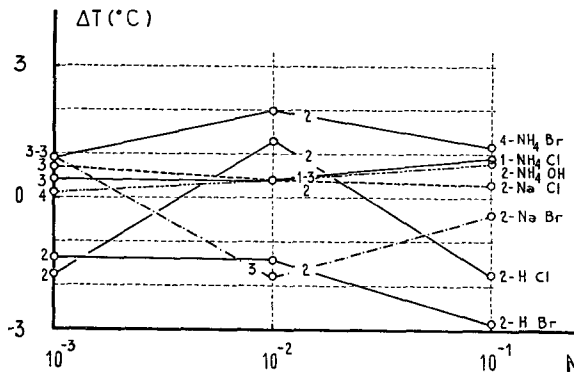


FIG. 7. Influence of the concentration for different electrolytes.

oils instead of silicone.¹ It may be concluded that the vapors of the alcohol used in the apparatus could not affect the measurements with water or electrolytic solutions.

4. Discussion

Influence of ions. The water used as a solvent in our experiments is not of the purest type and its mean freezing temperature has been always well above -40°C . It has been suggested (Mason, 1957, p. 135) that in this case the water probably contains a spectrum of insoluble freezing nuclei active at different temperatures. We shall discuss our results on the basis of this assumption.

We can imagine two ways in which the electrolyte ions may influence the mean freezing temperature. (i) They may induce nucleation by orienting the water molecules around them and thus favoring the formation of an embryo of critical radius, or (ii) they may increase or decrease the free energy change necessary for the formation of a critical embryo on the foreign nuclei (heterogeneous nucleation), either because the ions are adsorbed on the surface of the foreign nuclei or simply because the critical embryos are large enough to contain some of the ions, or for both reasons.

Moreover, the influences of the ions in each electrolyte pair are not independent from each other, as becomes obvious from observing the curves of Figs. 4 through 7 for different electrolytes with a common ion. We may nevertheless assume that this interaction disappears when the concentration becomes sufficiently low. We shall assume that this is already approximately true for 10^{-3} N.

It is easy to see that the hypothesis (i) can hardly

¹ The lack of influence of alcohol in our measurements is not in disagreement with the results of Brewer and Palmer (1951). The condition of the experiments made by these authors did not allow the measurement of the alcohol concentration; however, according to the lowering of the *melting* point of their droplets, these should have acquired concentrations much greater than the molar during the repeated melting and freezing.

be maintained if we are to adhere to Mason's hypothesis. In the first place, in all cases in which $\Delta T > 0$, one should expect that r' and not ΔT , would be independent of τ . In the second place, the negative values of ΔT could not be explained without assuming that there also is an influence on the heterogeneous freezing of the solvent. Thirdly, for sufficiently low concentrations, the values of ΔT should be determined solely by the more active ions in the pair, which does not happen for 10^{-3} N solutions (see Table 2).

We shall therefore adhere to hypothesis (ii).

TABLE 2. Values of ΔT and ϵ for solutions 10^{-3} N. The values of ϵ (in 10^{-13} erg) have been obtained from Fig. 9, for $\sigma = 18$ erg \cdot cm $^{-2}$. For each electrolyte, $\epsilon_{\text{add}} = \epsilon_{\text{cation}} + \epsilon_{\text{anion}}$.

ϵ_i	5.9 F $^-$	-1.7 Cl $^-$	0.3 Br $^-$	8.3 I $^-$	-2.0 OH $^-$	ϵ_i
Li $^+$ -3.0	0.6 2.9 2.9	-0.9 -4.1 -4.7	-0.7 -2.7 -2.7	1.6 5.1 5.3		ΔT ϵ ϵ_{add}
Na $^+$ -0.9	1.4 3.9 5.0	-0.7 -1.8 -2.6	0.9 1.4 -0.6	1.7 6.1 7.4	-0.9 -3.1 -2.9	ΔT ϵ ϵ_{add}
K $^+$ -1.5	1.2 4.4 4.4	-1.9 -3.5 -3.2	-0.8 -2.0 -1.2	1.9 8.1 6.8		ΔT ϵ ϵ_{add}
NH $_4^+$ 2.7	3.2 10.0 8.6	0.5 2.1 1.0	0.9 2.3 3.0	2.5 9.0 11.0	0.1 1.0 0.7	ΔT ϵ ϵ_{add}
H $^+$ -1.7	2.0 4.3 4.2	-1.7 -5.0 -3.4	-1.4 -3.2 -1.4	6.8 11.0 6.6	— — —	ΔT ϵ ϵ_{add}

Theory of heterogeneous nucleation. The rate of nucleation on a spherical nucleus may be expressed by the relation (see for instance Fletcher, 1958):

$$J_1 = K(R) \cdot \exp(-\Delta G/kT), \quad (3)$$

where J_1 is the number of embryos formed on each nucleus of radius R per second, $K(R)$ is a kinetic coefficient which depends on the surface of the nucleus, ΔG is the free energy change of formation of the embryo, and k is Boltzmann's constant. $K(R)$ may be put equal to $4\pi R^2 \cdot 10^{25}$; this value is uncertain within several orders of magnitude, but J_1 is much less sensitive to this uncertainty than to the dependence on ΔG .

We make now the assumption that the nuclei present in the water are completely "wet" by the ice phase; i.e., that the contact angle between ice and nucleus is zero. In this case the activity of the nucleus depends only on its radius R , and the critical free energy change is

$$\Delta G = \frac{4}{3}\pi \Delta G_v (r^3 - R^3) + 4\pi\sigma (r^2 - R^2). \quad (4)$$

Here $\Delta G_v = -\rho_h \cdot \Delta H_f \cdot T_s/M \cdot T_0$ is the free energy difference per unit volume for freezing (ρ_h = density of

ice; ΔH_f = enthalpy of fusion; M = molecular weight; T_0 = equilibrium freezing temperature), σ is the surface free energy for the ice-water interface, and $r = -2\sigma/\Delta G_v$ is the critical radius of the embryo.

Introducing (4) into (3) and computing J_1 as a function of T_s , it may be seen that it remains negligible until a certain value, after which it increases abruptly. We may then assume that each kind of nucleus becomes suddenly active at a supercooling $T_s = \tau$. We shall also assume that the spectrum of nuclei may be represented by

$$N = b \cdot \exp(\kappa\tau), \quad (5)$$

where N is the concentration of nuclei active at any temperature $\leq T_0 - \tau$ (Mason, 1957, p. 136). As is known, this distribution explains the experimental law (1). κ varies considerably from one sample of water to another. However, the following considerations will not be altered fundamentally by making the simplification $\kappa = 1$. Let us observe that the exponential increase of N means that most of the nuclei active in water at a certain value of T are those whose activation supercoolings are nearest to τ .² This allows us the further simplification of treating the nuclei active at each value τ as having a uniform size. R becomes thus an average value for the nuclei whose activation supercoolings are close to τ . Within these approximations the parameter τ may now be identified with the mean freezing supercooling defined in the experimental part.³

The total rate of nucleation in water at τ will be given by

$$J = N \cdot J_1 = b \cdot K(R) \cdot \exp\left(-\frac{\Delta G}{kT} + \tau\right), \quad (6)$$

where J is the number of embryos formed per unit time and unit volume. The coefficient b may be estimated from (5) and the approximate equation $V \cdot N = 0.5$ (where V is the droplet's volume and 0.5 means 50 per cent chance of freezing; see for instance Langham and Mason, 1958) as $\sim 10^3 \cdot e^{-\tau}$ cm $^{-3}$ for droplets of 1-mm diameter.

The value of R depends on the parameter τ , characteristic of the water sample, and if J is known, R may be computed from (4) and (6) by successive approximations. The value of J may be taken as giving a rate of nucleation of one embryo per second in the droplets observed.⁴ The results are shown in Fig. 8 for several plausible values of σ , which is not well known. For

² For instance, there are as many nuclei which become active between τ and $\tau+1$ as between 0 and τ .

³ This approximate treatment considers all the droplets as freezing simultaneously at the supercooling τ , and it implies that the rate of cooling could have no influence on τ .

⁴ J varies very rapidly and a difference of few orders of magnitude in its value is immaterial.

comparison, the value of the critical radius is $r = 20.8\sigma/\tau$ Å.

If a solution of an electrolyte in the same water (i.e. with the same nucleus spectrum) freezes at a different temperature T' , we assume that the difference is due to the effect of the ions on the critical free energy change, which is altered by the amount ϵ :

$$J = b \cdot K(R) \cdot \exp\left[-\frac{\Delta G' - \epsilon}{kT'} + \tau\right]. \quad (7)$$

We may put $J = \text{const.}$ for both samples considered (water and solution). Therefore, from (6) and (7)

$$\epsilon = \Delta G' - \frac{T'}{T} \Delta G, \quad (8)$$

ΔG is a function of R , τ and τ' . Here $\Delta G' = \Delta G'(R, \tau', \tau)$, where R remains the same, since it is the same water. τ' will be the critical radius for τ' . It may be assumed that the ions will not alter appreciably the structure of the interface ice-solution; τ' may then be taken as having the same value $-2\sigma/\Delta G_v(\tau')$ as for pure water.

Introducing the expression (4) in (8), we obtain

$$\epsilon = \left(A \frac{\tau + \tau'}{\tau^2 \tau'^2} + \frac{B}{T} R^2 - CR^3 \right) \Delta T, \quad (9)$$

$$A = \frac{16}{3} \pi \sigma^3 \left(\frac{MT_0}{\rho_h \Delta H_f} \right)^2,$$

$$B = 4\pi\sigma,$$

$$C = -\frac{4\pi\rho_h\Delta H_f}{3MT_0},$$

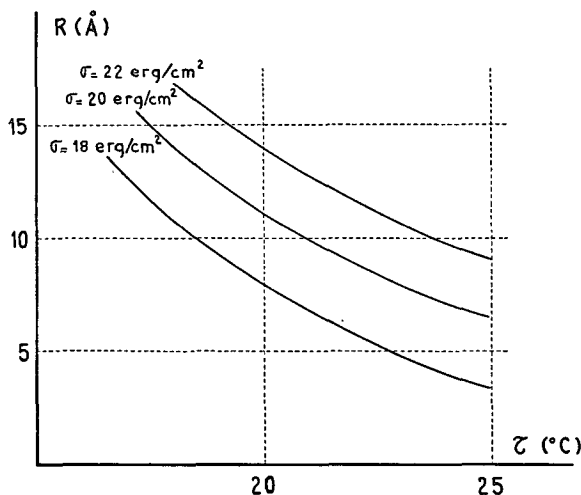


FIG. 8. Relation between the radii of nuclei and their activity.

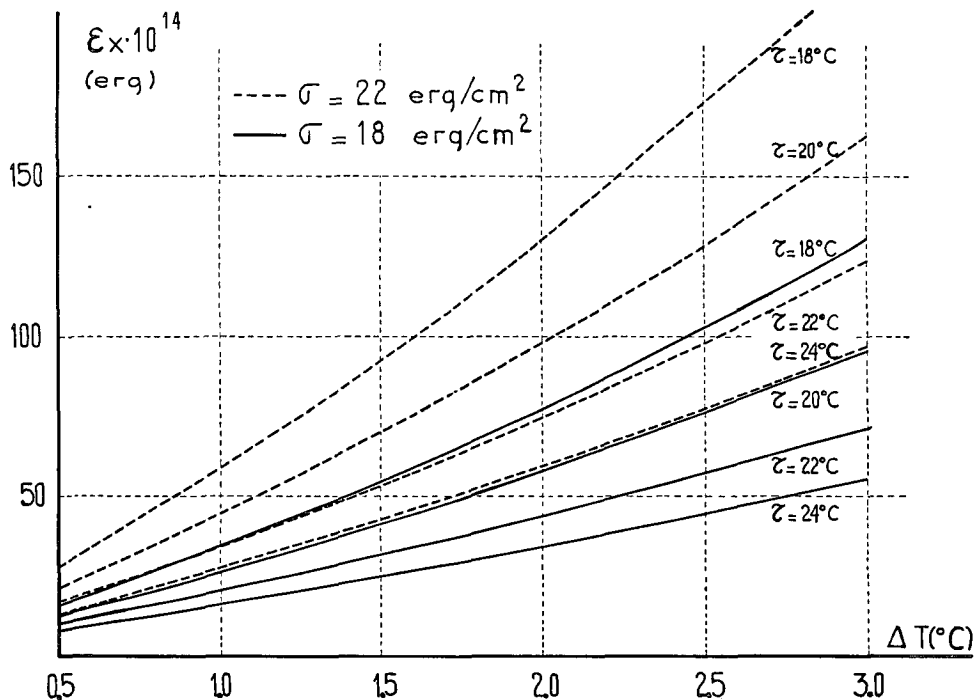


FIG. 9. Variation of the critical free energy change due to the presence of ions.

ϵ is roughly proportional to ΔT . It also depends on the variable τ and is rather sensitive to the value of σ . In Fig. 9, ϵ is plotted against ΔT for different values of τ and σ .

We recall now our assumption that for the more diluted solutions the ions act independently of each other, so that the effect of the electrolyte may be computed as the sum of the effects of the cation and the anion. In Table 2 are summarized the values of ΔT and ϵ for solutions of concentration 10^{-3} N and for $\sigma = 18$ erg/cm². Values ϵ_i have been assigned to the different ions in such a way that the sums $\epsilon_{\text{add}} = \epsilon_{\text{cation}} + \epsilon_{\text{anion}}$ may reproduce as well as possible the values of ϵ for the different electrolytes. The values of ϵ_i contain an arbitrary constant, which may be added to the whole series of cations and subtracted from the anions.

It may be seen that the results are consistent with the hypothesis of additivity within the limits of the experimental errors.

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