

ACCELERATION OF OXIDATION-REDUCTION REACTIONS IN FREEZING SOLUTION

NORIMICHI TAKENAKA, AKIHIRO UEDA and YASUAKI MAEDA

*Department of Applied Material Science, College of Engineering, University of Osaka Prefecture,
1-1 Gakuen-cho, Sakai 593*

Abstract: In general, most chemical reactions are accelerated at higher temperature, while reactions of which activation energy is negative are accelerated at lower temperature. The reaction rates, however, become much slower in the ice phase because molecule cannot move easily. It was found that a few reactions of which activation energies were positive were accelerated in freezing aqueous solution. The reaction rates in the freezing process were 10 to 10^5 times faster than those in solution at 25°C. The reaction occurred faster at faster freezing rate. Further, the reaction by freezing did not accelerate when the solution was frozen while stirring. It is proposed that the acceleration effect was based on the electrostatic concentration effect caused by ion separation.

1. Introduction

Many substances dissolved in aqueous solution are considered to be preserved by freezing. When an aqueous solution containing dilute electrolytes is frozen, an electric potential generates between the ice phase and the liquid phase (WORKMAN and REYNOLDS, 1950; LODGE *et al.*, 1956). They noted that the sign and magnitude of the electric potential depended on the concentration and kinds of electrolytes and the freezing rate. HATLEY *et al.* (1986a, b) observed that chemical reactions in aqueous solution were accelerated at subzero temperature and concluded that the acceleration was due to freeze concentration. Finnegan *et al.* (1991) pointed out that the reaction of sulphide with H₂O to form sulphate and H₂ took place in freezing in a cloud chamber when ice crystals grew, and also other endothermic reactions took place, and concluded that the reaction took place in a thin liquid layer next to the ice surface at -15°C. However, they did not detect H₂ nor other products except sulphate. Further, they discussed the theory of freezing reaction based on their results without considering other possibilities such as contaminants from the chamber and reactions on ice, in ice, in gas phase and so on. We have showed that the reaction of nitrite with dissolved oxygen was abnormally accelerated in freezing solution (TAKENAKA *et al.*, 1992). The reaction was not affected by the method and rate of thawing, light in the laboratory, or addition of pure ice. Further, we found that a few other oxidation reduction reactions were also accelerated in freezing solution by adjusting the conditions, such as pH or concentrations of reactants or additives. The reactions which did not proceed in solution did not proceed in freezing. In

this symposium we report the ratios of the reaction rates by freezing to the same reactions in solution and about the mechanism of the acceleration by freezing. The reactions in freezing will be very important in environmental chemistry.

2. Experiment

Reagent-grade chemicals were obtained from Wako Pure Chemicals Inc. and used without further purification. NaNO_2 was dried at 120°C for one night. Milli-Q water (resistance >18 Mohm cm) was used to prepare sample solution. The concentration of dissolved oxygen was adjusted by bubbling $\text{O}_2(99.95\%)/\text{N}_2(99.995\%)$ mixture gas obtained from Iwatani Gas Co. for more than 30 min in a thermostat. When H_2O_2 was used as an oxidant, all solutions were bubbled with N_2 gas for more than 30 min to remove dissolved oxygen. The pH of the solution was adjusted with sulphuric acid or hydrochloric acid just before freezing. Species in the ice were analyzed after thawing. Anions and Fe^{2+} were determined by ion chromatography (Yokogawa Analytical Systems Inc. IC-7000 Ion Chromatographic Analyzer) and the o-phenanthroline method, respectively, and pH was measured with a pH meter.

An aliquot of the solution (usually 3 ml) was drawn into a polyethylene syringe (75 mm \times i.d. 15 mm) sealed with a septum (free from gas phase) to hold the concentration of dissolved oxygen constant, and the syringe was then immersed in the coolant. The method of freezing and the material used for the reaction vessel did not affect the analytical results as described in the previous work (TAKENAKA *et al.*, 1992).

In order to compare the reaction rates in solution and in freezing, the reaction rates in solution were measured at the same concentration as those in freezing, and the same products or reactants were analyzed. The reaction in freezing started a few minutes later from the sample was immersed in the coolant, and then the rate increased gradually. Therefore, the rate in solution and in freezing were defined as the maximum rates.

3. Results

3.1. Various reactions accelerated by freezing

Some reactions in freezing were investigated by comparing with those in solution. Table 1 shows the reactions accelerated by freezing and also some of the reactions which were not accelerated or did not occur in freezing solution. All reactions by freezing which FINNEGAN *et al.* (1991) proposed were endothermic reactions and never occurred in solution. In our results, however, the reactions which did not occur in solution did not occur by freezing.

Only a few reactions were accelerated by the freezing-thawing process of aqueous solution as also shown in Table 1. Since it is not clear that the reaction mechanisms in solution and in freezing are the same, the rate constants could not be compared but the formation rates of products or decomposition rates of reactants were compared.

Table 1. Rates of reactions in freezing and in solution.

Oxidants mmol dm ⁻³	Reductants mmol dm ⁻³	pH	Rate (mol dm ⁻³ s ⁻¹)		Ratio Rf/Rs
			Rf ^{a)}	Rs ^{b)}	
O ₂	CH ₃ CHO		NR		
H ₂ O ₂	CH ₃ CHO		NR		
O ₂	Fe(II)		NR		
O ₂	S(-II)		NR		
O ₂	NH ₃		NR		
H ₂ O ₂	NH ₃		NR		
O ₂ , 0.253	N(III), 0.1	4.5	2.51 × 10 ⁻⁷	1.29 × 10 ⁻¹²	1.95 × 10 ⁵
H ₂ O ₂ , 1.32	N(III), 0.1	4.5	2.98 × 10 ⁻⁷	1.53 × 10 ⁻⁹	195
O ₂ , 1.9	S(IV), 0.1	7.8	7.92 × 10 ⁻⁸	3.92 × 10 ⁻⁹	20.2
H ₂ O ₂ , 1.32	S(-II), 0.1	9.6	1.96 × 10 ⁻⁷	2.60 × 10 ⁻⁹	75.4
H ₂ O ₂ , 0.013	Fe(II), 0.01	4.4	1.06 × 10 ⁻⁷	3.37 × 10 ⁻⁹	320

a) Rate by freezing. Freezing rates were 1.3 g/min for the reaction of Fe(II) with H₂O₂ and 0.2 g/min for the other reactions. NR means no reaction.

b) Rate in solution. Temperatures of the reactions was 4°C for the reactions of S(IV) with O₂, 15°C for Fe(II) H₂O₂ and 25°C for the others.

The reaction of nitrite (NaNO₂) with H₂O₂ in solution was relatively fast compared to that with dissolved oxygen. At low pH such as 3.0 or 2.5, the reactions in solution were very fast, and it was difficult to compare the reaction rates in solution and in freezing. In other words, in the reaction in freezing, the reaction in solution (when concentration of salts and pH were adjusted and the frozen sample was thawed completely) could not be neglected at low pH. At pH 4.5 the reaction in freezing to produce nitrate was about 195 times faster than that in solution.

The reactions of sulphite (Na₂SO₃) with dissolved oxygen in solution and also in freezing did not proceed at higher pH than 9.5, and were very slow at low pH. The fastest reaction rate in freezing to produce sulphate was obtained at pH 7.8, and it was about 20 times faster than that in solution (the fastest reaction rate was obtained at almost the same pH).

Sodium sulphide did not react with dissolved oxygen in freezing but reacted with H₂O₂ at pH 9.6 in freezing to produce sulphate and small amounts of sulphite, and the rate was about 75 times faster than that in solution.

The reaction of ferrous (FeSO₄) with dissolved oxygen was very slow at low pH but very fast at high pH in solution and was not accelerated by freezing. The reaction of ferrous sulphate with H₂O₂ was accelerated by freezing. The reaction at pH 4.4 was 320 times faster than that in solution.

The ratios of Rf/Rs in Table 1 are comparisons of the reaction rates. In order to evaluate the acceleration effects exactly, the reaction rate constants or the half lives of reactants should be compared. However, it is important to clarify what reactions and/or under what conditions the reactions are accelerated by freezing. Many reactions can be accelerated in freezing solution by adjusting conditions such as pH, reagent concentration, kinds of oxidants or reductants,

added salts, freezing rate, and so on. To clarify the acceleration mechanism the reaction of nitrite with dissolved oxygen was investigated in detail and will be discussed in the next section.

3.2. Reaction of nitrite with dissolved oxygen

In order to compare the reaction rate in freezing with that in solution, the reaction in solution and reactive species were investigated. The rate constant obtained at 25°C was $102 \pm 24 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ at pH 3.0, in good agreement with that ($72 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$) obtained at pH 1–4 by DAMSCHEN and MARTIN (1983) who investigated the reaction of nitrite with oxygen by analyzing dissolved oxygen at 25°C and who presented the rate expression as:

$$-d[\text{O}_2]/dt = 36[\text{HNO}_2]^2[\text{O}_2] (\text{mol dm}^{-3} \text{ s}^{-1}), \quad (1)$$

$$d[\text{NO}_3^-]/dt = -2d[\text{O}_2]/dt = -d[\text{HNO}_2]/dt. \quad (2)$$

The reaction rates in solution were investigated at various temperatures. Figure 1 shows the Arrhenius plot of the reaction of nitrite with dissolved oxygen. The activation energy obtained from the slope of the line was $50.8 \pm 2.0 \text{ kJ mol}^{-1}$. The reaction in solution of which activation energy was positive was much accelerated by freezing (at lower temperature). Further, in the supercooled state at -2 to -8°C , no NO_3^- was formed.

In the freezing process the following expression was obtained at pH 3–4.5 and freezing rate of 0.2 g min^{-1} (TAKENAKA *et al.*, 1992),

$$d[\text{NO}_3^-]/dt = 0.4[\text{nitrite}]_0[\text{O}_2]_0 (\text{mol dm}^{-3} \text{ s}^{-1}). \quad (3)$$

Here the subscript 0 denotes the initial concentration. The rate was almost

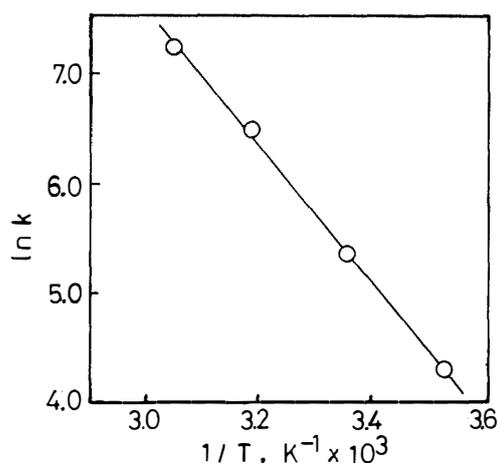


Fig. 1. Arrhenius plot for the reaction of nitrite with dissolved oxygen in solution. The regression line is $\ln k = (25.13 \pm 0.087) - (6110 \pm 242)/T$. The correlation coefficient is 0.999.

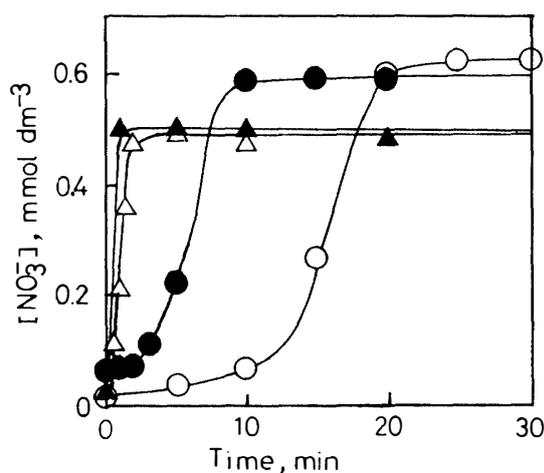


Fig. 2. Time profile of NO_3^- formation at various freezing rates. Temperature of the coolant: (\blacktriangle): -196°C , (\triangle): -78°C , (\bullet): -35°C , (\circ): -21°C . $[\text{nitrite}]_0 = 7.25 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{O}_2]_0 = 1.9 \times 10^{-3} \text{ mol dm}^{-3}$, pH 3.0

independent of the initial pH value. The faster the freezing rate, the faster was the reaction rate as shown in Fig. 2. In the Fig. 2, the initial NO_3^- was formed when oxygen was bubbled at pH 3.0 but it did not affect the reaction.

It is well known that when ice is formed the substances contained in the solution are rejected from the ice and concentrated into the solution. Hence we investigated the time profile of concentrations of ions (Na^+ , NO_2^- , NO_3^- , SO_4^{2-} and H^+) in solution and ice by sucking off the solution completely from the system. Although the reproducibility was not so good, the tendency of the time profile of separation of all ions between ice and solution was in agreement. The ion concentrations in the solution were only a few times higher than those in the ice phase.

4. Discussion

HNO_2 is well known to form NO and NO_3^- by disproportionation in solution. The time-courses of concentrations of nitrite and NO_3^- in solution were investigated in the absence of oxygen. Under our experimental conditions, within several tens minutes the disproportionation reaction can be negligible. Since the rate constant we obtained with ion chromatography was in good agreement with that obtained by measuring dissolved oxygen, we can evaluate the reaction rate in the solution with ion chromatography under our experimental conditions. One of the most important results was the positive value of the activation energy, that is, the reaction of nitrite with oxygen is slower at lower temperature. Therefore, the fact that the reaction of nitrite with dissolved oxygen in freezing solution was abnormally accelerated is not due to the effect of the temperature.

In eq. (3) the reactive species was represented as nitrite ($\text{HNO}_2 + \text{NO}_2^-$). The dependences of concentrations of NO_2^- and HNO_2 were investigated under pseudo-first order conditions. As shown in Figs. 3 and 4, the reaction rate by freezing was independent of NO_2^- concentration from 3.44×10^{-5} to 1.37×10^{-2} mol dm⁻³ 5.6 at 1×10^{-4} mol dm⁻³ of HNO_2 , while it shows a 0.5 order dependence on HNO_2 concentration from 7.30×10^{-7} to 2.91×10^{-4} mol dm⁻³ at 1×10^{-4} ,

$$d[\text{NO}_3^-]/dt = k[\text{HNO}_2]_0^{0.5}[\text{O}_2]_0 \text{ (mol dm}^{-3}\text{s}^{-1}\text{)}, \quad (4)$$

mol dm⁻³ of NO_2^- as shown in eq. (4) (HNO_2 and NO_2^- concentrations were calculated from pH value and the equilibration constant). The kinetic order of the reaction for the initial concentration of HNO_2 contradicts that for initial concentration of nitrite (see eqs. (3) and (4)). In order to investigate this contradiction, the maximum reaction rate was estimated. The reaction by freezing takes place around the interface of the ice and the solution, because: (I) no reaction occurred in the ice, (II) the reaction became slower at low temperature in the solution and (III) the concentration effect to the solution by freezing was only a few times. The reaction is expected to take place with ice growth. We calculated the maximum reaction rate assuming that the ion concentrations in the

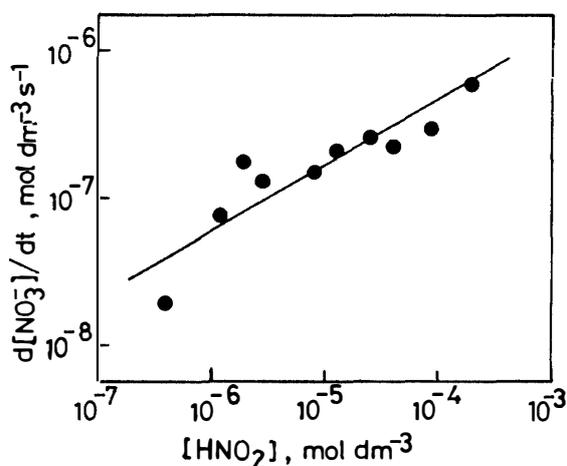


Fig. 3. The formation rate of nitrate to the initial concentration of HNO_2 . The freezing rate was 0.2 g min^{-1} . The initial concentrations of NO_2^- and dissolved oxygen were 1.0×10^{-4} and $2.5 \times 10^{-4} \text{ mol dm}^{-3}$, respectively. The correlation coefficient of the line is 0.905 and the slope is 0.46.

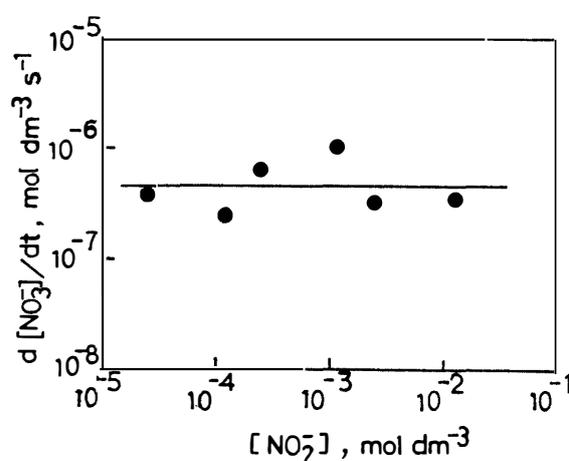


Fig. 4. The formation rate of nitrate as a function of the initial concentration of NO_2^- . The freezing rate was 0.2 g min^{-1} . The initial concentrations of HNO_2 and dissolved oxygen were 1.0×10^{-4} and $2.5 \times 10^{-4} \text{ mol dm}^{-3}$, respectively. The slope of the line is 0.015.

system was uniform in ice and solution (in other words, no concentration effect by freezing occurred) and all HNO_2 molecules in the ice formed are oxidized to NO_3^- . Table 2 shows the calculation results. The first to third columns are the data used when the HNO_2 dependence was obtained. The fourth column is the maximum NO_3^- formation rates calculated with the above assumption. The fifth column is the observed NO_3^- formation rates, and the last column is the ratio of the observed rate (B) to the calculated maximum rate (A). The results indicate that the observed rates (B) are 2–77 times faster than the maximum rates (A). In other words, the reactants were concentrated. Further, the ratios B/A are different at the different HNO_2 concentration. This means that 0.5 order dependence on HNO_2 concentration may be doubtful. Figure 2 shows that the amounts of NO_3^- formed at faster freezing rate are less than those at slower freezing rate. This result suggests that at slower freezing rate the chemical reaction was faster than the freezing rate because: (I) the amount of NO_3^- formation was less in spite of the faster reaction rate and (II) it is considered that the unreacted nitrite is incorporated into ice at faster freezing rate. In other words, the ice formation is the rate-determining step at slower freezing rate, and the rate of freezing is comparable with the reaction rate at faster freezing rate. Therefore it is difficult to obtain the kinetic order of the reaction. However HNO_2 is considered to be the reactant since little NO_3^- formed at high pH (at pH 5.6 99.3% is NO_2^- and 0.7% is HNO_2).

The reaction of nitrite with dissolved oxygen by freezing is not accelerated by a photochemical, a catalytic or an electrochemical reactions. One of the most important results was that the reaction by freezing did not accelerate when the solution was frozen with stirring. Here we discuss about the mechanism of the

Table 2. Ratio of the observed reaction rate and calculated maximum rate of NO_3^- formation.

(1)	(2)	(3)	(4)	(5)	(6)
$[\text{HNO}_2]$ mol dm^{-3}	$[\text{NO}_2^-]$ mol dm^{-3}	pH	$d[\text{NO}_3^-]_{\text{max}}/dt$ $\text{mol dm}^{-3} \text{ s}^{-1}$ (A)	$d[\text{NO}_3^-]_{\text{ob}}/dt$ $\text{mol dm}^{-3} \text{ s}^{-1}$ (B)	B/A
7.3×10^{-7}	1.0×10^{-4}	5.6	8.1×10^{-10}	3×10^{-8}	30
1.5×10^{-6}	1.0×10^{-4}	5.3	1.6×10^{-10}	9×10^{-8}	60
2.9×10^{-6}	1.0×10^{-4}	5.0	3.2×10^{-9}	2.50×10^{-7}	77
4.6×10^{-6}	1.0×10^{-4}	4.8	5.1×10^{-9}	1.55×10^{-7}	30
9.2×10^{-6}	1.0×10^{-4}	4.5	1.0×10^{-8}	2.11×10^{-7}	21
1.5×10^{-5}	1.0×10^{-4}	4.3	1.6×10^{-8}	2.61×10^{-7}	16
2.9×10^{-5}	1.0×10^{-4}	4.0	3.2×10^{-8}	4.26×10^{-7}	13
4.6×10^{-5}	1.0×10^{-4}	3.8	5.1×10^{-8}	3.24×10^{-7}	6.3
9.2×10^{-5}	1.0×10^{-4}	3.5	1.0×10^{-7}	4.91×10^{-7}	4.8
2.9×10^{-5}	1.0×10^{-4}	3.0	1.6×10^{-7}	7.59×10^{-7}	2.3

Column (1)–(3): Initial conditions of experiment.

Column (4): The maximum rates of NO_3^- formation calculated with assuming that no concentration effect occurred (the concentrations of nitrite in the ice and the solution are the same) and all HNO_2 molecule incorporated in the ice formed are oxidized to NO_3^- .

Column (5): Experimental results obtained in this work.

Column (6): Ratio of (5)/(4).

The freezing rate was 0.3 g min^{-1} , and the sample volume was 3 cm^3 .

acceleration effect. WORKMAN and REYNOLDS (1950) reported that a generation of potential differences started when freezing started, and stopped when freezing stopped. Further, FINNEGAN *et al.* (1991) pointed out that the reaction in the growing ice crystal took place by separation of ions and the resulting electric effect. The electric potential, however, is not directly related to the acceleration (TAKENAKA *et al.*, 1992). The electric potential is generated by ion separation and affects the ion mobilities and electrochemical effects, but the acceleration cannot be completely explained by the electric potential. HATLEY *et al.* (1986a, b) reported that some reactions were accelerated at subzero-temperature in the undercooled state and that the driving force of the acceleration was the concentration effect, that is, about $1 \times 10^{-3} \text{ mol dm}^{-3}$ was concentrated to 1–10 mol dm^{-3} , in spite of the supersaturation.

The ion concentration effect is probably caused by ion separation, and our results indicated only a few times concentration. All anions were rejected by the ice, but Na^+ was relatively less rejected, and an electric current was obtained from ice to solution. Therefore, the positively charged ice phase (also produced by ion separation) attracts anions to the ice-solution interface (electrostatic effect); anion concentration is expected to become much higher at the interface but not in solution.

Because nitrous acid is a weak acid, it is expected that nitrite ions around

the interface will bond easily with H^+ of H_2O in the ice or interface to form HNO_2 which reacts with dissolved oxygen. In this situation the term "concentration effect" is not suitable, because the ion concentration is produced not only by the concentration effect but also by the electrostatic effect. It can be considered that anions are weakly fixed at the interface of the ice and the solution by the mixed electric and the concentration effects. The observed concentration effect on the solution when the sample was frozen with stirring (no reaction occurred) was larger than that when it was frozen without stirring (reaction occurred). It is considered that stirring disperses HNO_2 weakly fixed at the interface by the electric effect into the solution.

Nitrate ion formation occurred later than ice formation, probably for the following reason. When the rejection of ions by ice is stronger than the electrostatic force of attraction, nitrite ion cannot approach the interface. When the rejection by ice exceeds a certain threshold, the electrostatic force of attraction becomes stronger and nitrite ion can approach the interface.

As mentioned above, the freezing process can provide a new path way for the chemical reaction. The reactions shown in Table 1 take place only under some conditions such as pH value and kinds and concentrations of substances (reactants and additives). Freezing rate could be one of the conditions. The reactions which are accelerated by freezing and the conditions under which they are accelerated need to be investigated to clarify the acceleration mechanism.

The fact that freezing, which is a simple physical process, accelerates chemical reactions is not widely known. In the environment, the reaction by freezing is considered to take place in the following situations: (I) formation of cumulonimbus; (II) freezing of rain drops, for example rain falls to the radiation cooled ground in winter; (III) formation of snow and rime. It is supposed that freezing plays an important role in environmental chemistry because it is a normal process in the environment.

References

- DAMSCHEN, D. E. and MARTIN, L. R. (1993): Aqueous aerosol oxidation of nitrous acid by O_2 and O_3 and H_2O_2 . *Atmos. Environ.*, **17**, 2005–2011.
- FINNEGAN, W. G., PITTER, R. L. and YOUNG, L. G. (1991): Preliminary study of coupled oxidation-reduction reactions of included ions in growing ice crystals. *Atmos. Environ.*, **25A**, 2531–2534.
- HATLEY, R. H. M., FRANKS, F., DAY, H. and BYTH, B. (1986a): Subzero-temperature preservation of reactive fluids in the undercooled state. I. The reduction of potassium ferricyanide by potassium cyanide. *Biophys. Chem.*, **24**, 41–46.
- HATLEY, R. H. M., FRANKS, F. and DAY, H. (1986b): Subzero-temperature preservation of reactive fluids in the undercooled state. II. The effect on the oxidation of ascorbic fluids in the undercooled state. *Biophys. Chem.*, **24**, 187–192.
- LODGE, J. P., BAKER, M. L. and PIERRARD, J. M. (1956): Observations on ion separation in dilute solutions by freezing. *J. Chem. Phys.*, **24**, 716–719.
- TAKENAKA, N., UEDA, A. and MAEDA, Y. (1992): Acceleration of the rate of nitrite oxidation by freezing in aqueous solution. *Nature*, **358**, 736–738.

WORKMAN, E. J. and REYNOLDS, S. E. (1950): Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relationship to thunderstorm electricity. *Phys. Rev.*, **78**, 254–259.

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