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A critical examination of a cryochemical method for the preparation of high surface area semiconducting powders

Part 2 *Non aqueous solvents. The behaviour of solid solutions in freeze drying*

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A solid solution which is sublimed under vacuum during the preparation of a high surface area powder will melt if the temperature of the surface is greater than the eutectic temperature, irrespective of the initial concentration of the solution.

Three criteria may be used in selecting a suitable solvent for freeze drying: (1) For solvents whose surface temperatures are considerably below the eutectic temperature a small value of the latent heat of sublimation is desirable; or for those whose melting points limit the heat input, a high equilibrium vapour pressure at the melting point is required. (2) A low freezing point depression. (3) A high solubility of the solute. Acetic acid was shown to be a useful solvent for preparing Co_2NiO_4 spinel. A computer model of the drying process was modified to take account of added solutes and solvents other than water.

1. Introduction

In an earlier paper [1] the vacuum sublimation of ice, a time consuming step in the freeze drying process, was studied with a view to increasing the rate of sublimation. Heating the ice increases this rate, but the temperature of the ice must not exceed its melting point A mathematical model of vacuum sublimation was constructed in which the heat flow to the subliming surface (by natural processes or from an external heat source) was balanced by the heat required for sublimation; and the resulting mass flow from the surface balanced by pumping along tubes of known conductance to a liquid nitrogen trap.

The temperature of the ice surface was determined by the heat and mass balance for a given heat input and the maximum heat which could be supplied to the surface without melting was calculated.

In this way, it was shown theoretically and experimentally that for a particular experimental geometry, the time taken to sublime 100 g ice fell from 40 h, when only heat from the surroundings was allowed to reach the surface, to 4 h, when 0.7 W cm^{-2} were supplied by an i.r. lamp.

In this paper the model has been extended to include different solvents, the effect of a solute is discussed and guide lines for choosing suitable solvent-solute systems are developed.

2. Theory

2.1. Melting points of solid solutions

The mathematical model described earlier showed that, providing the capacity of the pumping system is adequate (this is usually the case in a well-designed system) the maximum rate of sublimation is reached at the highest possible surface temperature, i.e. the melting point of the

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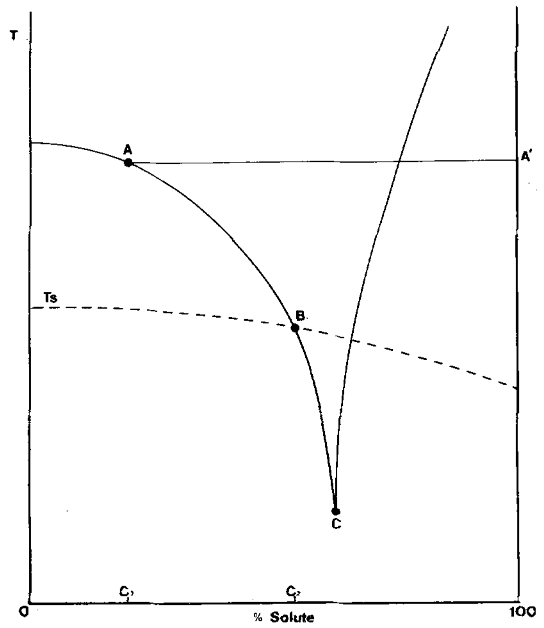

Figure 1 Surface temperature of a subliming solution superimposed on the melting point curve for a non-volatile solute in solution. For explanation of symbols see text.

solution. It is thus of interest to study the melting points of rapidly frozen solutions, and the effect on the melting point of the initial concentration of solute.

Consider a dilute solution (e.g. an ionic salt in water) of concentration C_1, which is rapidly frozen, and the solvent sublimed under vacuum. The temperature of the subliming surface (T_s) is determined by the heat input and characteristics of the solvent, and remains approximately constant during sublimation. It is assumed that at the concentration C_1, $T_s < T_m$ where T_m is the melting point. As the drying process continues, the loss of solvent leaves the remaining solid solution notionally more concentrated, until at some new concentration C_2, melting temperature T'_m, $T_s = T'_m$, and the frozen solution may melt. It is possible, however, that the concentration of the bulk frozen solution remains at C_1, with solid solute separating out. In this case, the melting point of the frozen solution will always remain at that corresponding to the initial concentration (T_m). This is shown in Fig. 1. The dashed line T_s, represents the temperature of the surface during drying, and A–A′ is the constant melting point of the solution discussed in the second case, in which the dried solute does not interact with the solid solution. The line A–B–C is the equilibrium freezing point curve with eutectic C. Thus if the solution becomes more concentrated during sublimation (i.e. it reaches equilibrium), melting will occur at B. It is seen that to avoid melting at any stage, the line of T_s must not cross the freezing point curve.

To test these possible courses of sublimation a series of aqueous solutions were frozen and vacuum dried.

2.2. Computer model of vacuum sublimation

The theory of the model used to describe vacuum sublimation is given in an earlier paper [1]. Here we extend the model to solvents other than water and investigate the effect of added solutes.

TABLE I Parameters for computer model of drying process. Apparatus: Radius of flask = 6.34 cm, pumping tube radius = 1.5 cm, length = 2.5 cm, vapour temperature = 293 K, and trap temperature = 77 K.

Solvent	Latent heat[a] of sublimation (mol^{-1})	Density of solid (g cm^{-3})	Viscosity[b] of vapour (μP)	Molecular weight (g mol^{-1})	A[c]	B
Water	50 900[d]	0.917[f]	96.0	18		
Acetic acid	40 780[d]	1.1[d]*	80	60	8.269[h]	−2130.2
Glycerol	110 758[g]	1.3[g]*	100	92	15.0177	−5785.6
Ethanol	49 173[g]	0.80[g]	60	46	12.266	−2568.6
DMSO	69 125[e]	1.1[e]*	80	78	12.2313	−3690.76

[a] Calculated (see text) from latent heat and C_p data.
[b] Extrapolated from tabulated data.
[c] $\log_{10}(P/\text{mm Hg}) = A + B/T$ (see text).
[d] Reference [4].
[e] Reference [5].
[f] Reference [6].
[g] Physical properties of hydrocarbon [7].
[h] $\log_{10}(P/\text{mm Hg}) = -2445.6/T + 8.23 \log_{10} T - 0.0168T + 1.205 \times 10^{-5} T^2 - 6.757$ [6].
*Estimated or extrapolated datum.

2.2.1. Sublimation of different solvents

The times taken to sublime 100 g of five solvents; water, acetic acid, dimethyl sulphoxide (DMSO), ethanol and glycerol, were calculated for two heating rates, first at a constant rate of 30 W (a typical experimental value), and secondly at the maximum heating rate. The parameters used in the calculation are given in Table I. Those for the vacuum system are of the experimental arrangement used in this work. Physical data were obtained from the literature where possible. The heat of sublimation (V) at the melting point was calculated from the heat of vaporization at the boiling point (ΔH_v), the heat of melting (ΔH_m) and specific heat data, using the Laws of Hess and Kirchoff:

$$V = H_m + H_v(C_p^v - C_p^s)(T_m - T_b) \quad (1)$$

where C_p^v and C_p^s are the specific heats at constant pressure of vapour and solid respectively, and are taken to be independent of temperature in the range considered. T_m and T_b are the melting and boiling temperatures of the solvent. The equilibrium vapour pressure above solid solvent at a temperature T (P_T) was derived from V and the tabulated triple point pressure and temperature (P^*, T^*) using the Clausius–Clapeyron equation:

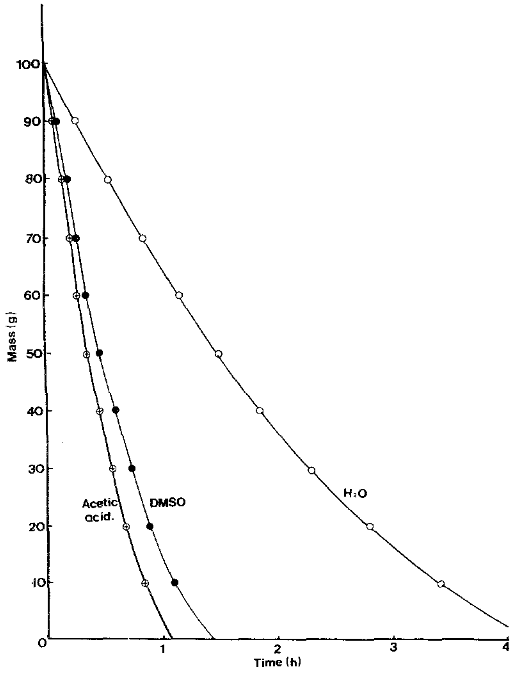

Figure 2 Calculated drying curves for 100 g solvent, sublimed under vacuum with heat supply of 30 W. ○, H_2O; ●, DMSO, ⊕ acetic acid.

TABLE II Calculated maximum drying rates for different solvents in the experimental apparatus

Solvent	Melting point (K)	Maximum heat input (W)	Maximum sublimation rate g sec^{-1}
Acetic acid	289	4000	0.575
Water	273	4800	0.166
DMSO	291.5	40	4.4×10^{-3}
Ethanol	156	0.0003	3×10^{-8}
Glycerol	293	0.002	1.6×10^{-8}

$$\log_{10}(P_T/\text{mm Hg}) = A + \frac{B}{T} \quad (2)$$

where $A = \log_{10}(P^*/\text{mm Hg}) + V/2.303RT^*$ $B = -V/2.303R$.

In Fig. 2 are calculated drying curves for 100 g water, DMSO and acetic acid, for an applied heat of 30 W. The model predicted that ethanol and glycerol should melt at this rate of heating. A second calculation was performed to determine the maximum heating rates possible with the different solvents. The results are given in Table II.

2.2.2. The effect of added solute

The effect of an added solute on the drying rate is two fold. First, the melting temperature is lowered as discussed above. The computer model was modified to take the melting point of a solution as the maximum possible temperature. Secondly the addition of solute causes a depression of the freezing point of the solvent. For low concentrations Raoult's Law is obeyed and the vapour pressure lowering is proportional to the mole fraction of solute. The calculated solvent vapour pressure was modified by multiplication by $1 - x_s$, where x_s is the mole fraction of solute, up to a maximum value of x_s corresponding to the mole fraction of solute at the eutectic. However the most concentrated solutions in water have mole fractions less than 0.1, which affect the model only slightly. For example, a calculated drying curve of a 10% sodium chloride solution in water leads to an increase in surface temperature, compared to pure ice, of 0.5° C. The effect was more marked with other solvents but was still relatively small.

3. Experimental

Sodium chloride and calcium chloride solutions in water were freeze dried to determine the effect of these salts on the melting point of the solid solutions. A sample of the spinel Co_2NiO_4 was prepared from nitrates dissolved in acetic acid to illustrate the use of a solvent other than water.

3.1. Freeze drying NaCl and $CaCl_2$ solutions

Analar sodium chloride or calcium chloride ($CaCl_2 \cdot 2H_2O$) was dissolved in deionized, distilled water. The solution was sprayed, as an aerosol, into liquid nitrogen to produce the frozen solution for vacuum sublimation.

A freeze drier, similar to the systems reported earlier [1, 2], was fitted with a 150 W infra-red lamp. A chromel–alumel thermocouple, screened from direct infra-red radiation, was positioned just at the surface of the frozen solution. A Pirani gauge measured the total pressure in the flask containing the frozen solution.

100 cm^3 of a solution containing a known weight of sodium chloride (5 to 20 wt %) or calcium chloride (10 to 30 wt %) was frozen and the water sublimed under vacuum (~0.05 Torr). The temperature of the surface was monitored and melting, if it occurred, noted. The composition of a melted solution was determined by evaporating water from a measured volume and weighing the resulting solid.

3.2. Freeze dried Co_2NiO_4 from acetic acid solutions

3.2.1. Materials

Analar $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in Analar glacial acetic acid.

3.2.2. Methods

12.4 g $Co(NO_3)_2 \cdot 6H_2O$ and 6.16 g $Ni(NO_3)_2 \cdot 6H_2O$ (sufficient for 5 g Co_2NiO_4) were dissolved in 40 cm^3 hot acetic acid. This solution was sprayed into liquid nitrogen and the acetic acid sublimed under vacuum in the apparatus above. A 150 W lamp gave 30 W on the initial surface, and a surface temperature of − 2° C to + 3° C, during the sublimation. The resulting solid was decomposed under vacuum in the same apparatus at 250° C for 3 h and cured in air at 400° C for 10 h.

The Co_2NiO_4 prepared by this method was characterized by X-ray powder patterns, a BET surface area determination was made and the conductivity of the powder measured [1]. A Teflon bonded Co_2NiO_4 electrode [3] was fabricated and tested for oxygen evolution. It is possible to compare these results with those obtained from a sample of Co_2NiO_4 prepared by freeze drying aqueous solutions of the nitrates.

4. Results

4.1. Freeze dried NaCl and $CaCl_2$ solutions

Solutions containing 5, 10, 15 and 20 wt % sodium chloride dried without melting. The temperature of the surface varied from − 20° C to − 33° C (± 3° C) during drying. It was noted that if the thermocouple was allowed out of the surface ice, the temperature of the dry sodium chloride was greater than 100° C, showing the existence of a marked temperature gradient between the frozen solution and solid sodium chloride.

Solutions containing 10, 20, 25 and 30 wt % $CaCl_2 \cdot 2H_2O$ were frozen rapidly and the ice vacuum sublimed. All solutions melted during sublimation. The composition of the melted solutions was the same, irrespective of the initial concentration. The literature value for the melting point [4] coincided with the experimental melting point. The results of this experiment are given in Table III. Fig. 3 shows the experimental surface temperatures of the different solutions superimposed on the eutectic diagram of the calcium chloride/water system [6].

TABLE III Initial and final (melted) concentrations of frozen solutions of calcium chloride subjected to vacuum sublimation

Wt % $CaCl_2 \cdot 2H_2O$ in 100 cm^3 water	Literature* m.p. (° C)	Surface temperature		Final composition wt % $CaCl_2$ (± 1)	Literature* m.p. (° C)
		Initial (° C) (± 3)	Final (° C) (± 3)		
10	− 3.9	−36	−28	26	−30
20	−11.5	−33	−33	26	−30
25	−16.3	−32	−27	26	−30
30	−22	−31	−30	25	−29

*From reference [4].

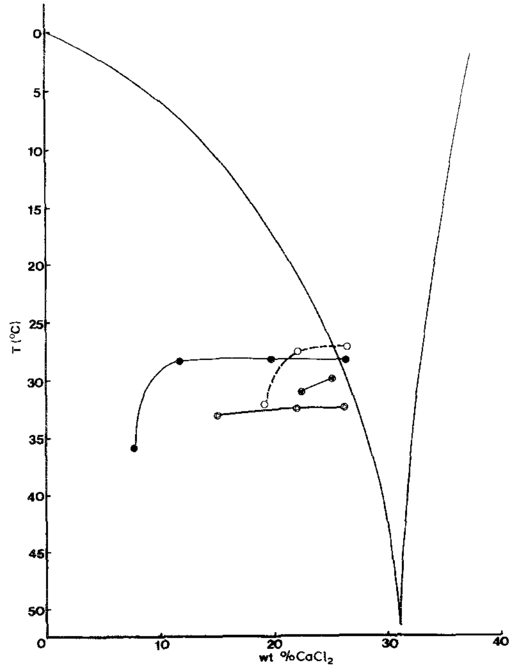

Figure 3 Surface temperature of frozen $CaCl_2/H_2O$ solution during vacuum sublimation, superimposed on the eutectic diagram for $CaCl_2/H_2O$. The final point on each curve is the temperature and composition of the melted solution. Initial wt% $CaCl_2 \cdot 2H_2O$: •, 10; ⊚, 20; ○, 25; ⊛ 30.

4.2. Co_2NiO_4 spinel prepared from nitrates in acetic acid

The preparation time, physical properties and effectiveness as an oxygen electrode of Co_2NiO_4 prepared by freeze drying from acetic acid solution, are compared with the results from a sample prepared from aqueous solution in Table IV. It was found that it is not possible to use an infra-red lamp to its full advantage when drying aqueous solutions of cobalt and nickel nitrates because of melting during vacuum sublimation. There was no restriction on the use of external heat when using acetic acid as solvent.

5. Discussion

5.1. The melting points of frozen solutions

The results of the experiments with frozen sodium chloride and calcium chloride solutions, show conclusively that vacuum sublimation of frozen aqueous solutions leads to a concentration of the solutions as postulated above. The effect is akin to that produced by spreading salt on ice to cause melting except that here, sublimation of ice from a solution creates its own salt.

As the solvent sublimes the local surface concentration increases to the maximum solubility of the solute. If the temperature of the surface, which is determined by the rates of heating and sublimation is above the melting point of the frozen solution, local melting will occur. The resulting solution will be made more dilute by the dissolution of the less concentrated bulk solution, and when its melting point reaches the temperature of the surface, the solution will re-freeze. This process continues until the entire solid solution has reached that concentration, the melting point of which corresponds to the surface temperature. At this point the frozen solution melts. It is clear from the above discussion that any solution will eventually melt if the temperature of the surface is above that of the eutectic. Thus in the experiments conducted above, a surface temperature of -30° C was above that of the calcium chloride/water eutectic (-52° C) but below that of the sodium chloride/water eutectic (-21° C).

5.2. The role of the solvent in freeze drying

5.2.1. The rate of sublimation

The rate of removal of solvent vapour is determined, for a given pumping system, by the presence of vapour above the subliming surface. This in turn may be shown to be related to the equilibrium vapour pressure at the temperature of the surface, and the heat input.

If the pressure above the surface is P_g, and the

TABLE IV Properties of Co_2NiO_4 spinel freeze dried from solutions of the nitrates in acetic acid and water

Method of preparation	Preparation time for 5 g (h)	Conductivity (Ω^{-1} cm^{-1})	BET surface area (m^2 g^{-1})	X-ray powder pattern	Oxygen reduction current at $\eta = 0.7$ V* (mA cm^{-2})
Freeze dried from acetic acid	3.5	10	34	spinel	80
Freeze dried from water	70	10	42	spinel	100

*Measured in 5 N KOH at 25° C, air. Reference electrode – dynamic hydrogen electrode (DHE), i.r. corrected.

temperature of the vapour T_g, the number of moles striking 1 m^2 of surface is $P_g(2\pi MRT)^{-1/2}$ sec^{-1} where M is the gram molecular weight of the solvent. The number of moles evaporating from the surface is given by a similar expression containing the equilibrium vapour pressure P_e and the temperature of the surface T_s, vis: $P_e(2\pi MRT_s)^{-1/2}$ sec^{-1}. The net evaporation rate is the difference between these expressions and is equal to the number of moles subliming, given by $H/(V \times A)$ where H is the heat input, V the latent heat of sublimation and A, the area of the surface. Therefore

$$P_g = P_e(T_g/T_s)^{1/2} - H(2\pi MRT_g)^{1/2}(V \times A)^{-1} \quad (3)$$

For a system at constant heat input, the rates of sublimation of different solvents are dependent on the heat of sublimation, assuming the melting point has not been exceeded. If the maximum heat input is attained, when the subliming surface is at its melting point, the rate is better calculated, (in the absence of the value for the heat input) using Equation 3 for P_g, from the pumping characteristics of the system. In this case inspection of Equation 3 reveals that the dominating factor is the equilibrium vapour pressure at the melting point. Table V contains vapour data for five solvents at their melting points. Using this criterion for the rate of sublimation at the maximum heating rate, acetic acid is the optimum solvent with ethanol and glycerol having very low vapour pressures. A more accurate test is given by the computer model of maximum sublimation rates (Table II) which takes account of different heats of sublimation and of the variation of vapour pressures with temperature. It is seen however that the results agree with the order of solvents (acetic acid > water > DMSO ≫ ethanol ≈ glycerol) suggested by the values of equilibrium vapour pressures at the melting point. It must be noted however that the maximum heating rates calculated for acetic acid and water could not be realised in practice. Of interest is that the melting temperature of a solvent is not a useful guide to the rate of sublimation.

TABLE V Vapour pressure data for different solvents

Solvent	Melting point (K)	Vapour pressure of solid at m.p. (mm Hg)	Reference
Water	273	4.58	[6]
Acetic acid	289	7.91	[6]
Glycerol	293	1.9×10^{-5}	[7]
Ethanol	156	6.3×10^{-5}	[7]
DMSO	291.5	0.37	[5]

5.2.2. Guidelines for choosing a suitable solvent

Three factors determine the optimum solvent for a given solute: (1) the rate of sublimation of the solvent at a given heat input; (2) the maximum depression of the freezing point; (3) the solubility of the solute near room temperature.

(1) Solvents may be divided into two classes: those which, under normal heating conditions ($<1\,W\,cm^{-2}$) have a surface temperature below the melting point of the solution (class A); and those for which the heat input is limited by the melting temperature of the solution (class B). Of the solvents discussed here acetic acid is a class A solvent, and ethanol and glycerol are class B. Water and DMSO are normally class A, but for solutes which cause a great depression of the freezing point (e.g. $CaCl_2$ in water) they may fall into class B. For solvents in class A, the rate of sublimation at a given heat input is solely determined by the heat of sublimation. Thus the relative rates of sublimation of acetic acid, DMSO and water seen in Fig. 2 are explained. Class B solvents, however, are best compared by their equilibrium vapour pressures at the melting point of the frozen solution as discussed above.

(2) The importance of the freezing point depression is seen in the use of water as a solvent. For many solutes water acts as a class A solvent and the possible heat input is not limited. However a solute which causes a great depression in the freezing point may effectively rule out water as a solvent. For example, the equilibrium vapour pressure of ice at −52° C (the calcium chloride/water eutectic point) is 0.023 mm Hg, which may be compared with the value at 0° C of 4.58 mm Hg, a difference of some 200 times.

(3) The solvent with the greatest ability to dissolve a given solute is preferred when considering this factor. However it must be noted that a high solubility may also lead to an increased lowering of the melting point.

Experience has shown that although acetic acid cannot dissolve as great a quantity of ionic salts as water, the increase in sublimation rate outweighs this factor, and acetic acid has proved to be a most useful solvent.

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