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

Part 1 *Rate of freeze-drying*

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In the preparation of high surface area powders by the method of freeze-drying, a solution of the dissolved substance is rapidly frozen in liquid nitrogen, followed by vacuum sublimation of the ice. A computer analysis of the vacuum sublimation step showed that the heat supply to the surface ice was less than that for maximum sublimation. An infra-red lamp was used to supply extra heat and, in agreement with the computer model, the time required for sublimation of 100 g ice fell from 42 h to 3.8 h. The ice did not melt. Conductivity measurements of samples of freeze dried 10 at % Li doped $NiSO_4$ prepared with and without the extra heat supply showed that in both cases, a very uniform distribution of Li^+ in the $NiSO_4$ lattice had been achieved. The surface areas of the freeze-dried samples were 3 times that of a sample of 10 at % Li doped $NiSO_4$ which had been prepared by boiling to dryness a solution of $LiSO_4$ and $NiSO_4$.

1. Introduction

The recent and growing interest in semiconducting oxides as electro-catalysts has shown the need for a method of preparation yielding high surface area powders having the correct structures and properties. Conventional methods of preparation of oxides containing more than one metal ion involve high temperature calcining to ensure sufficient inter-diffusion of the ions. However, at these elevated temperatures sintering occurs, with resultant loss of surface area.

Tseung and Bevan [1] have shown that the use of a cryochemical technique, "freeze-drying", leads to atomic mixing of the precursor metal salts which, after decomposition, allows a lower temperature for calcining. A drawback of this method, as reported by Tseung and Bevan, is the time required to produce relatively small amounts of catalyst (approximately 4 days for 10 g oxide).

In this paper, we analyse the drying process to determine the slowest step and give a method by which the drying time may be reduced to a few hours.

1.1. The cryochemical method

If a solution containing the salts of two different metals is cooled rapidly, freezing will occur without fractional crystallization thus retaining the random ordering of ions of the solution. This state of subdivision and degree of homogeneity will be retained if the ice is sublimed under vacuum, since the solutes are effectively immobilized by the ice crystals during the drying process. For oxide preparations the subsequent decomposition of the salts may also be performed *in vacuo*.

For example, a mixture of the freeze-dried nitrates of lanthanum, strontium and cobalt (II) may be decomposed at 300° C and 10^{-2} torr and sintered at 550 to 600° C to give the correct perovskite structure of $La_{0.5}Sr_{0.5}CoO_3$ with a surface area of $30\,m^2\,g^{-1}$ [2], whereas conventional techniques involving thermal decompo-

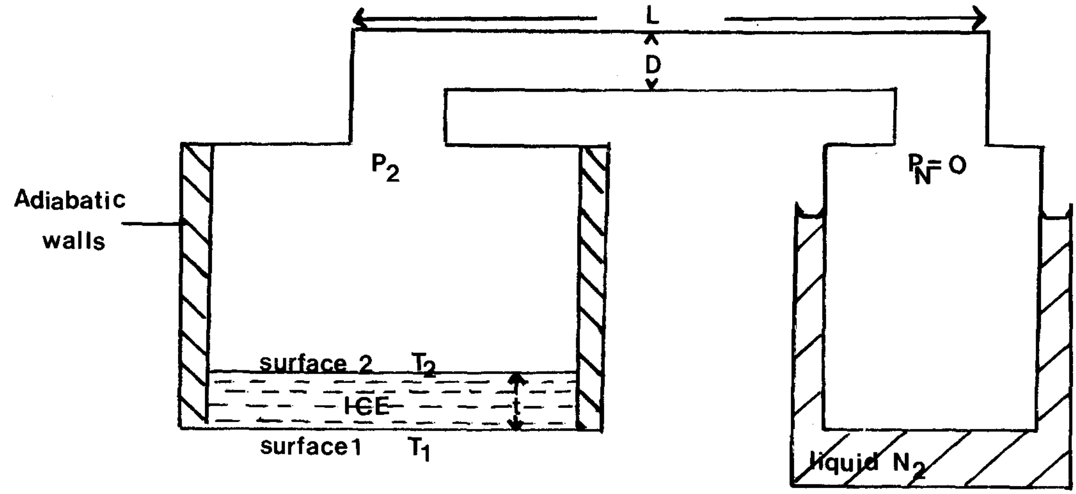

Figure 1 Schematic diagram of the vacuum drying apparatus.

sition of the mixed nitrates and subsequent solid state reaction to form the oxide would require temperatures of over 1000° C, leading to low surface areas. This technique has been used to prepare high surface area cermet and alloy powders [3], $MgO–Al_2O_3$ powder [4] and a variety of semiconducting oxides e.g. lithiated NiO [1] and $NiCo_2O_4$ [5].

1.2. Improvements in the freeze-drying process

The slowest step of the procedure to prepare oxide catalysts in the sublimation of ice from the frozen salt solution. However, to increase the rate, heat may not be supplied indiscriminately because of the possibility of melting and fractionation of the solution.

Certain factors involved in the drying of various biological materials have been noted [6], and the application of heat to increase the rate of sublimation has been used. However, the optimum rate of heat supply is usually determined empirically.

2. Analysis of the drying process

The analysis will be carried out via an examination of the steady state heat balance and mass balance of the system illustrated schematically in Fig. 1.

2.1. The supply of heat

In the absence of any external heating, heat will reach the ice from the surroundings by convection and radiation to the surface of the vessel (surface 1) followed by conduction through an ice layer to the subliming surface (surface 2). Radiation from the surroundings to surface 2 may also occur.

2.1.1. Convective heat supply to surface 1

If surface 1 is at temperature T_1 and of area A and the room temperature is T_R, then [7]

$$H_{\text{conv}} = hA(T_R - T_1) \qquad (1)$$

where H_{conv} is the rate of convective heat supply to surface 1, and h is the heat transfer coefficient. For free convection in air within the normal freeze-drying temperature range and with a downward-facing, square, cold plate of side L m [7],

$$h = 0.02139((T_R - T_1)/L)^{1/4}\ \text{W K}^{-1}\text{m}^{-2} \qquad (2)$$

2.1.2. Radiative supply of heat to surface 1

The rate of radiative heat supply to surface 1 (R_1) is given by Stefan's Law;

$$R_1 = A\sigma(\alpha T_R^4 - T_1^4) \qquad (3)$$

σ is Stefan's constant (5.67×10^{-8} W m^{-2} K^{-4}), and α is the absorptivity of surface 1 (numerically, for wet ice at 273 K, α is 0.97).

2.1.3. Conduction of heat from surface 1 to surface 2

If the thermal conductivity of the frozen solution is k, the cross-sectional area is A and the thickness t, then

$$H_{\text{cond}} = kA/t(T_1 - T_2) \qquad (4)$$

where H_{cond} is the rate of heat flow from surface 1 to surface 2.

2.1.4. Radiative heat supply to surface 2

This may also be evaluated from Stefan's Law as in Section 2.1.2;

$$R_2 = A\sigma(\alpha T_{\mathrm{R}}^4 - T_2^4) \tag{5}$$

2.1.5. The steady state flow of heat

At the steady state, the flow of heat to surface 1 must be equal to the rate of conduction to surface 2, thus;

$$H_{\mathrm{cond}} = H_{\mathrm{conv}} + R_1. \tag{6}$$

The total heat supply to surface 2, H_{s} is therefore,

$$H_{\mathrm{s}} = H_{\mathrm{cond}} + R_2 \tag{7}$$

$$= H_{\mathrm{conv}} + R_1 + R_2 \tag{8}$$

2.2. Loss of heat from surface 2

Under steady state conditions, all the heat supplied to surface 2 must be lost, and the mechanism for the loss of heat is sublimation. The rate of sublimation, S, may be determined from the rate of heat loss, H_1, and the heat of sublimation, L, of the solvent;

$$S = H_1/L \tag{9}$$

2.3. The mass balance

2.3.1. Loss of solvent from surface 2

At a given partial pressure of solvent over surface 2, P_2, the rate of sublimation may be calculated from kinetic theory. The rate of condensation of solvent on 1 m^2 of surface per second, C_2, is;

$$C_2 = P_2/(2\pi RMT_{\mathrm{g}})^{1/2}, \tag{10}$$

where M is the molecular weight of the solvent and T_{g} is the temperature of the gas phase solvent molecules. It is assumed that every molecule hitting surface 2 condenses.

The rate of sublimation, S_2, from surface 2 at temperature T_2 is derived from the equilibrium vapour pressure of the frozen solvent (P_{eq}) at that temperature;

$$S_2 = P_{\mathrm{eq}}/(2\pi RMT_2)^{1/2}. \tag{11}$$

The net sublimation rate is, therefore;

$$S = S_2 - C_2 \tag{12}$$

2.3.2. Pumping away solvent vapour

The solvent vapour is pumped exclusively by liquid nitrogen traps whose speed for condensible gases is 15 l sec^{-1} [8] for 1 cm^2 of trap surface. Rotary oil pumps serve to reduce the background pressure of air. The pumping system is thus represented (see Fig. 1) by a pressure gradient between the surface of the ice (partial pressure P_2) and the cold trap at a partial pressure of solvent vapour P_{N}. For most solvents P_{N} is very small (e.g. ice at 77 K has a vapour pressure of $<10^{-7}$ torr) and may be taken as zero. The flow of vapour, F, is fixed by the dimensions of the apparatus and the pressure gradient (P_2).

Assuming mixed molecular and viscous flow, which cover the range of pressures encountered in this work, the vapour flow rate F for water is, in g sec^{-1} [8];

$$F = \frac{P_2}{RT_{\mathrm{R}}} \left[0.188\frac{D^4}{L}P_2 + 15.554\frac{D^3}{L}\frac{(1 + 2.067 \times 10^{-4}DP_2)}{(1 + 2.542 \times 10^{-4}DP_2)}\right] \tag{13}$$

Where D is the diameter in cm and L the length of the tube in cm through which the flow is taking place, at a pressure difference of P_2 torr.

2.4. Calculation of model parameters

P_2, T_1 and T_2, and hence the rate of sublimation and heat flow may be determined from the above equations and the constraints, (a) for heat flow through surface 1;

$$H_{\mathrm{cond}} = H_{\mathrm{conv}} + R_1, \tag{14a}$$

(b) for heat flow through surface 2;

$$H_{\mathrm{s}} = H_1 \tag{14b}$$

(where H_1 is the heat lost from surface 2 by sublimation) and (c) for the mass flow in the system;

$$F = S. \tag{15}$$

There being no analytical solution, a numerical method has been devised and implemented on an ICL 1900E and CDC 7600 computer.

Two binary search routines are used to determine T_1 and T_2. At a given T_2 a binary search routine for T_1 (between the limits $T_1 = T_2$ and $T_1 = T_{\mathrm{R}}$) is used to bring $H_{\mathrm{conv}} + R_1 - H_{\mathrm{cond}} = 0$. The value of the heat supply H_{s} from Equation 7 is equated to H_1 (Equation 14) and thus S (Equation 9) can be calculated. For water as solvent the equilibrium vapour pressure of ice at

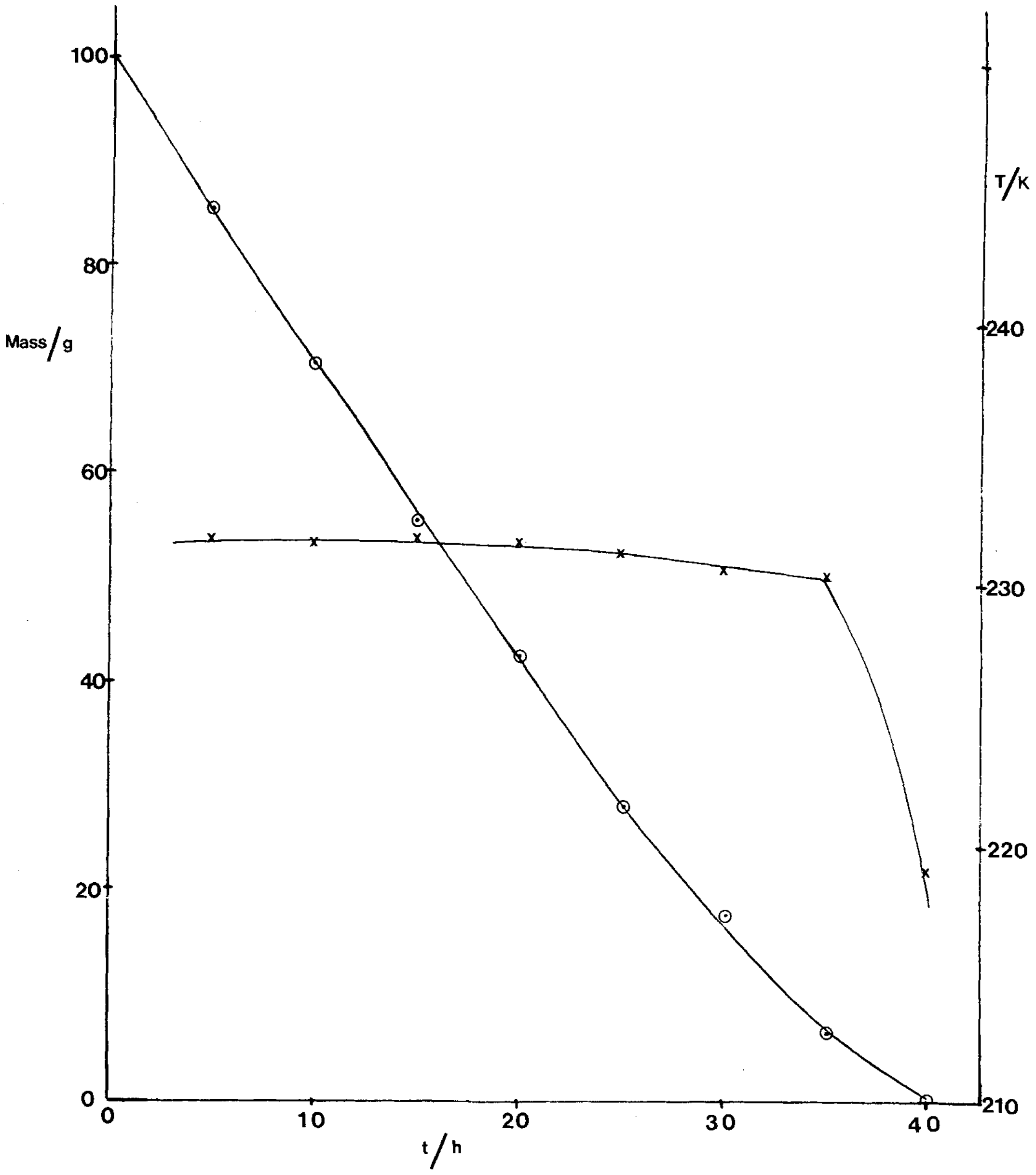

Figure 2 Results of a computer model of the vacuum drying process for 100 g ice. No external heat supplied. Left ordinate, ⊙ mass of ice remaining. Right ordinate, X temperature of the subliming surface, (T_2).

temperature T_2 is given by [9]

$$\log_{10} P_{\text{eq}} = -\frac{2445.6}{T_2} + 8.23 \text{ antilog}_{10} T_2 - 0.0168\, T_2 + 1.205 \times 10^{-2} T_2^2 - 6.757 \qquad (16)$$

From Equations 10, 11, 12 and 16, P_2 may be calculated from S, and used to determine the flow F from Equation 13. The function $F-S$ is calculated. T_2 is varied by the binary search routine between the melting point of the frozen solution and an arbitrary low value (taken as 150 K) until $F-S=0$. A system which tries to converge on a value for T_2 which is greater than the melting point of the solution is deemed to have melted.

To take account of the reducing size of the ice block the procedure is operated for a number of short time intervals, Δt. At the steady state flow, the amount of solvent evaporated in time Δt is $S\Delta t$. The thickness of the ice block is recalculated

TABLE I Dimensions of the freeze-drying apparatus and input parameters for the computer model.

Pumping tube	diameter = 2.0 cm length = 15.0 cm
Ice block	diameter of spherical flask = 6.8 cm thickness of ice block = 2.12 cm initial area of ice = 40 cm^2
Latent heat sublimation of ice	46643 J (g mol)$^{-1}$
Thermal conductivity of ice	0.021 W cm^{-1} K^{-1}

and the entire procedure repeated to find new values of T_1, T_2, P_2 etc. In this way, the time to sublime a given quantity of frozen solvent may be determined.

The computer program was written to accommodate a spherical flask containing the frozen solution (as was used in practice), and a supply of heat to surface 2 from an external source. In the latter case, the heat supply H_s is fixed and no longer depends on the conduction–convection–radiation mechanism described above.

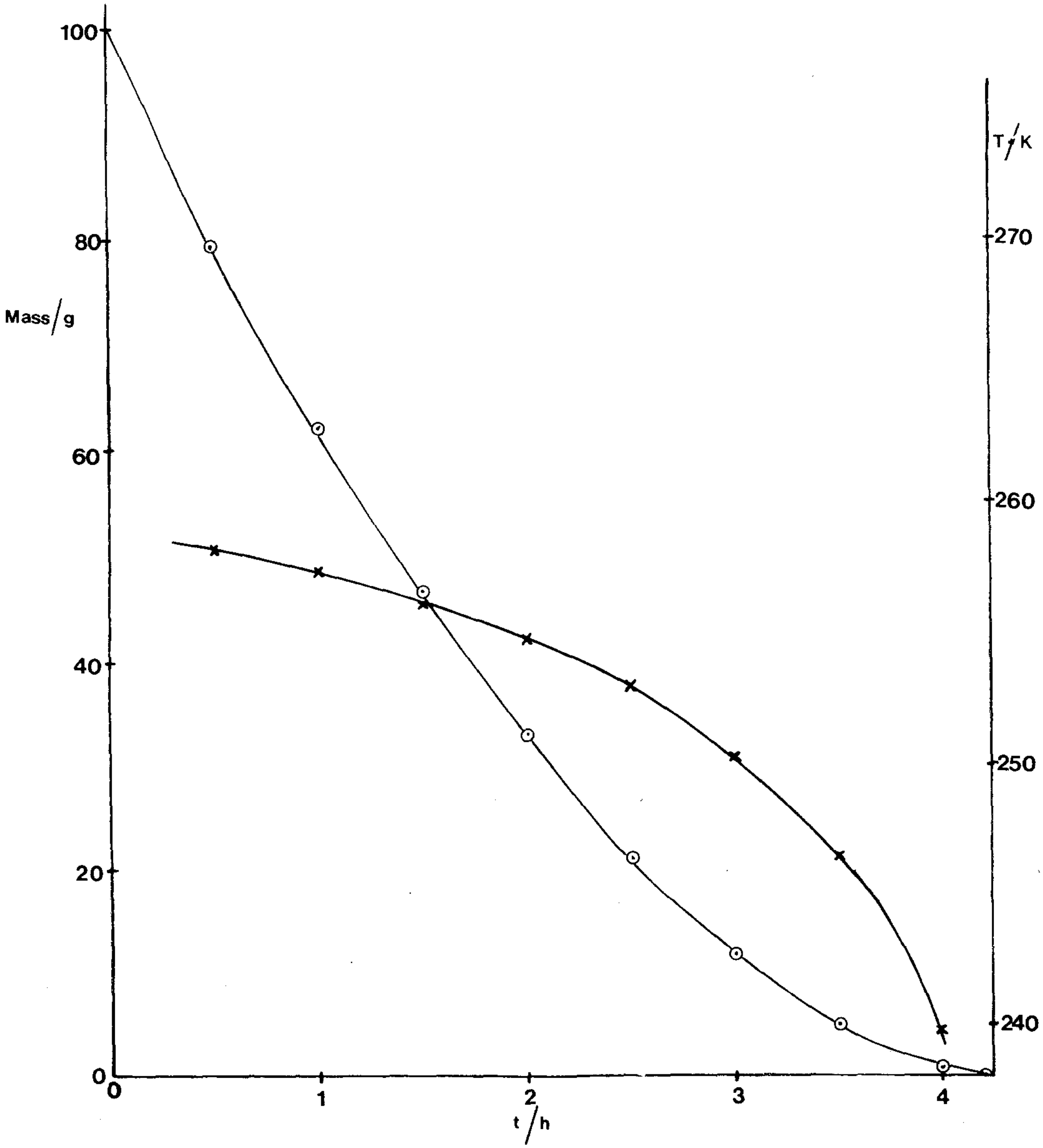

Figure 3 Results of a computer model of the vacuum drying process for 100 g ice. 0.7 W cm^{-2} heat supplied to the ice surface. Left ordinate, ⊙ mass of ice remaining. Right ordinate, X temperature of the subliming surface, (T_2).

2.5. Results of the computer model

Table I contains the parameters used in calculating the time taken to sublime 100 g ice. The dimensions of the flask and pumping tube were taken from the experimental apparatus. Fig. 2 shows the predicted rate of sublimation and the temperature of the surface T_2, during the process.

For the maximum rate of sublimation, T_2 should be near the melting point of the frozen solution in order to maximize P_{eq} in Equations 11 and 12. Fig. 2 shows that for heat supplied from the room alone by convection, conduction and radiation, the rate of sublimation is much less than could be possible. The surface of the ice was calculated to be receiving no more that $0.05\,\mathrm{W\,cm^{-2}}$, whereas the computer model showed that up to $2.4\,\mathrm{W\,cm^{-2}}$ could be supplied without melting. This was calculated by increasing the heat supplied for a given pumping speed until T_2, the temperature of the ice surface, reached 273 K. We found for the arrangement in Table I, a heat supply of 98 W on a $40\,\mathrm{cm^2}$ surface resulted in a value of T_2 of 272.7 K. In calculating the limiting heat supply, the dimensions of the pumping tube exert a profound influence. If the diameter of the tube is reduced from 2.0 to 1.5 cm, the heat required to give $T_2 = 272.6\,\mathrm{K}$ is now 40.3 W.

Fig. 3 is calculated for the same system but with a constant heat supply of $0.7\,\mathrm{W\,cm^{-2}}$. The estimated time required to sublime 100 g ice falls from 40.3 to 4.2 h. Increasing the pumping speed by changing the dimensions of the apparatus was found to change the time of sublimation by only 5% for low levels of heating. Thus the model of the drying process suggests a major improvement would be brought about by supplying up to $2.4\,\mathrm{W\,cm^{-2}}$ to the surface of the frozen solution.

3. Experimental

3.1. Validity of the computer model

To test the model given above, 100 g ice were sublimed in a freeze-drying apparatus, first with no external heat and then with a 100 W infra-red lamp suspended above the ice surface giving, from the geometry of the arrangement, an irradiation of $0.7\,\mathrm{W\,cm^{-2}}$. The ice was held in a 250 ml round-bottomed flask. The dimensions of the tubes connecting the flask and liquid nitrogen trap are given in Table I. The background air pressure was kept below 5×10^{-3} torr by a $50\,\mathrm{l\,sec^{-1}}$ two-stage rotary oil pump.

3.2. Uniformity of mixing

To test the uniformity of ionic mixing produced by the freeze-drying process Tseung and Bevan [1] measured the conductivity of silver chloride doped with cadmium ions. The sensitivity of silver chloride to heat and light makes this system unsuitable for use in this case, and so nickel sulphate doped with lithium ions was investigated to observe the effect of an external source of heat. The conductivity of nickel sulphate rises by orders of magnitude as lithium ions are introduced into the lattice due to the formation of $\mathrm{Ni^{2+}/Ni^{3+}}$ couples. If, however, the lithium ions are not distributed uniformly throughout the lattice the conductivity will remain close to that of nickel sulphate. Fractionation caused by melting during the freeze-drying process will thus result in a marked reduction of conductivity of the final sample.

3.2.1. Preparation of freeze dried samples

AnalaR $\mathrm{NiSO_4 \cdot 6H_2O}$ and $\mathrm{Li_2SO_4 \cdot H_2O}$ were dissolved in 400 ml water to give 4 g of 10 at % $\mathrm{Li^+}$ doped $\mathrm{NiSO_4}$. The solution was sprayed as an aerosol into a dish containing liquid nitrogen which produced rapid freezing of the droplets. The solid sample was apportioned between two 250 ml round-bottomed flasks, both of which were connected to the vacuum system described above. The pressure in the system was monitored by an ionization gauge. Heat was supplied to the ice surface in one flask by a 100 W infra-red lamp, the second flask being shielded from the lamp. The time taken to dry both samples was noted. To remove bound water from all samples tested the dry powders were subjected to the infra-red lamp for 2 h in a vacuum of 10^{-2} torr. Control samples of $\mathrm{NiSO_4}$ and 10 at % lithiated nickel sulphate prepared by boiling to dryness a mixed solution, were prepared and tested.

3.3. Characterization of the freeze-dried samples

3.3.1. Surface area measurement

BET surface areas were determined from the adsorption of nitrogen at 77 K. A CI Electronics microbalance measured the increase of weight on adsorption of nitrogen with an accuracy of 1 μg. Corrections were applied for inherent imbalance, buoyancy and thermomolecular flow, and the cross-sectional area of nitrogen was taken as $16.2\,\mathrm{Å^2}$.

TABLE II Drying times for different heating rates and systems.

System	Weight solvent (g)	Heat supply	Drying time (h)	Computer prediction (h)
Ice	100	None	42	40.3
Ice	100	0.7 W cm^{-2} from i.r. lamp	3.8	4.2
10% $Li^+/NiSO_4$	200	None	80	–
10% $Li^+/NiSO_4$	200	0.7 W cm^{-2} from i.r. lamp	5	–

TABLE III Specific conductivity and surface area measurements of lithiated nickel sulphate, and nickel sulphate prepared by different methods.

System	Preparation	Specific conductivity (Ω^{-1} cm^{-1})	Surface area (m^2 g^{-1})
$NiSO_4$	Boiled to dryness	8.9×10^{-9}	–
10 at % $Li^+/NiSO_4$	Boiled to dryness	4.8×10^{-8}	5
10 at % $Li^+/NiSO_4$	Freeze-dried, no external heat	3.5×10^{-7}	14
10 at % $Li^+/NiSO_4$	Freeze-dried external heat 0.7 W cm^{-2}	4.0×10^{-7}	13

3.3.2. Conductivity measurement

A weighed sample of each powder was compressed at a pressure of 2000 lb in.$^{-2}$ between stainless steel electrodes in a glass tube (i.d. 3 mm, and approximate length of 25 mm). The conductivity of the sample was measured by an a.c. bridge.

4. Results

4.1. The sublimation of ice

The time taken to sublime 100 g of ice with and without external heating is given in Table II. Also shown are the computer model predictions and the time taken to dry the lithiated nickel sulphate samples.

4.2. Characterization of the freeze-dried samples

Table III contains surface area and conductivity data of 10 at % lithiated nickel sulphate samples prepared by boiling to dryness, and freeze-drying with and without an external heat source. It can be seen that the use of an external heat source does not affect the drying process or the quality of the dry powder.

5. Discussion and conclusions

The use of a theoretical model to describe the freeze-drying process has highlighted the slowest step – the supply of heat to the subliming surface – and has predicted the amount of heat which the surface may accommodate without melting.

The order of magnitude difference found in the conductivities of the samples of lithiated nickel sulphate prepared by boiling to dryness and both freeze-dried samples is sufficient proof that the use of an infra-red lamp to reduce the drying time does not lead to melting.

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