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Nucleation studies in supersaturated potassium dihydrogen orthophosphate solution and the effect of soluble impurities

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Nucleation rates as indicated by induction period have been studied for supersaturated solutions of potassium dihydrogen orthophosphate with and without the addition of soluble impurities in the temperature range 20 to 40° C. The effects of temperature, supersaturation and impurity content are reported. The interfacial tension, energy of formation and critical radius of nuclei of the crystal are calculated based on classical nucleation theory. The presence of soluble impurities enhances the nucleation rate of potassium dihydrogen orthophosphate crystals.

Nomenclature

ΔG	energy of formation of nucleus
B	a constant
J	frequency of formation of nuclei
k	Boltzmann constant
K	a constant
m	slope of line plot $\ln \tau$ against $1/\ln^2(x/x_0)$
N	Avogadro's number
R	gas constant
r	radius of sphere inscribed in the crystal nucleus in equilibrium with solution
T	temperature (K)
U_1	energy of activation for the molar transition from phase 1 (solution) to phase 2 (crystal)
v	volume per molecule in solid phase
V	molar volume of crystal
x	mole fraction of solute in the supersaturated salt solution at temperature t
x_0	mole fraction of solute in the salt solution saturated at temperature t
μ_1	chemical potential of supersaturated solution
μ_{10}	chemical potential of saturated solution
μ_r	chemical potential of nucleus of radius r
μ_α	chemical potential of nucleus of infinite radius
σ	interfacial tension of crystal
τ	induction period

1. Introduction

The interfacial tension between the crystal nuclei and the surrounding solution is the crucial parameter in comparing nucleation theory with experimental data. The classical homogeneous nucleation theory has been successfully tested for the nucleation of liquid droplets from vapour and from liquid solution and for crystal formation in melts [1–7]. The interfacial tension that could be calculated using nucleation theory in the above studies can be compared with values from macroscopic equilibrium measurements. In the nucleation of crystals from solution no such comparison can be made, since we have no means of obtaining values of the interfacial tension except through homogeneous nucleation. If we consider the theory as generally approved and applicable also to nucleation from solution, we may use homogeneous nucleation as a method for measuring interfacial tension [8, 9].

The formation of crystal nuclei from supersaturated solutions where none existed previously has been the object of many investigations. Spontaneous formation of crystal nuclei was

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reported [10, 11] to take place at temperatures below the saturation temperature, if sufficient waiting time was allowed. The presence of insoluble foreign crystals reduces the supersaturation required to form crystals from their solutions [12–16]. The addition of ionic impurities, especially Fe^{3+} and Cr^{3+}, may reduce the induction period considerably in aqueous solutions of inorganic salts [17]. The presence of soluble impurities increases the nucleation rate in supersaturated ADP solutions [18].

The rate of homogeneous nucleation (J) is indirectly computed by measuring induction period (τ) and taking $J \propto \tau^{-1}$ [19–22]. After preparing supersaturated solutions there is often a period where no phase change can be observed, the induction period; then minute nuclei appear and grow into visible crystals. In the present work, the induction period has been measured for supersaturated potassium dihydrogen orthophosphate (KDP) solution with and without the addition of soluble impurities. The experimental technique to measure the induction period is similar to that used by Mullin [23] and Joshi and Antony [9].

2. Theory

The following theoretical consideration can be used to calculate the interfacial tension, energy of formation and critical radius of the nuclei. The basic relationship of equilibrium between solid and its solution which connects the solubility expressed as the chemical potential to the particle size is the Thomson equation,

$$\mu_r - \mu_\alpha = \frac{2\sigma}{r} v \qquad (1)$$

When the crystal attains a radius r, it will be in equilibrium with the solution and under these conditions the chemical potentials of the two coexisting phases are equal. The free energy of formation of the nucleus of the new phase of radius r in equilibrium with its solution is expressed as

$$\Delta G = \frac{16\pi\sigma^3 v^2}{3(\mu_r - \mu_\alpha)^2} \qquad (2)$$

The frequency of formation of these crystal nuclei from their respective supersaturated solutions has been given as

$$J = K \exp\left(\frac{-U_1}{kT}\right) \times \exp\left(\frac{-\Delta G}{kT}\right) \qquad (3)$$

For a given volume of solution the frequency of formation of nuclei is inversely proportional to the induction period:

$$\ln\tau = \ln K^{-1} + \frac{U_1}{kT} + \frac{\Delta G}{kT} \qquad (4)$$

For an isotherm, the term U_1/kT is a constant and Equation 4 is written as

$$\ln\tau = B + \frac{\Delta G}{kT} \qquad (5)$$

The energy of formation ΔG can be evaluated from the change in chemical potential [24]

$$\mu_1 - \mu_{10} = \mu_r - \mu_\alpha = kT\ln(x/x_0) \qquad (6)$$

Applying Equations 2 and 6 in Equation 5

$$\ln\tau = B + \frac{16\pi\sigma^3 v^2}{3k^3T^3\ln^2(x/x_0)}$$

$$= B + \frac{16\pi\sigma^3 V^2 N}{3R^3T^3\ln^2(x/x_0)} \qquad (7)$$

Equation 7 suggests a straight line for $\ln\tau$ against $1/\ln^2(x/x_0)$ with the slope given by

$$m = \frac{16\pi\sigma^3 V^2 N}{3R^3T^3} \qquad (8)$$

The interfacial tension of the solid relative to its solution has been calculated from the slope of the line $\ln\tau$ against $1/\ln^2(x/x_0)$ as

$$\sigma = RT\left[\frac{3m}{16\pi V^2 N}\right]^{1/3} \qquad (9)$$

The energy of formation of a critical nucleus has been calculated from the experimental data as

$$\Delta G = \frac{RTm}{\ln^2(x/x_0)} \qquad (10)$$

In the light of the Equations 1 and 6 the radius of the nucleus in equilibrium with its solution has been computed as

$$r = \frac{2\sigma V}{RT\ln(x/x_0)} \qquad (11)$$

3. Experimental details

3.1. Apparatus

A Corning glass tube 15 mm in diameter fitted with an ebonite cork is used as nucleation cell. The nucleation cell is placed in a constant temperature bath, the temperature of which is thermostatically controlled to an accuracy of ± 0.01° C over a wide range of temperatures. A lamp placed at the rear of the bath illuminates the nucleation cells. The bath is large enough to accommodate many nucleation cells so that nucleation runs can be made side by side.

3.2. Materials

Recrystallized samples of Analar grade KDP powder and triple distilled water are used in the present study. Divalent anionic soluble impurities like potassium carbonate, potassium sulphate, potassium oxalate, sodium borate (borax) and potassium chromate of Analar grade are selected and used to study their effect in nucleating supersaturated KDP solutions.

3.3. Procedure

Aqueous solutions of KDP are prepared by dissolving the required amounts of KDP salt in 100 ml of triple distilled water at temperatures slightly higher than their respective saturation temperatures. The concentrations of the solutions thus give the required supersaturations at the experimental temperatures. Supersaturation is obtained by natural cooling. Experiments are performed at selected degrees of supersaturation and temperature. Several nucleation runs are carried out under controlled conditions. The time taken between the achievement of supersaturation and the first appearance of tiny crystals is measured as the induction period [25]. Reproducible results with an accuracy of ± 2% are obtained. A stock solution of desired impurity is prepared by dissolving 500 mg in 250 ml of triple distilled water. For a known concentration, the mass of impurity to be added with the KDP of a particular supersaturation at a particular temperature is calculated. The required volume of the stock solution containing the above calculated mass is taken and made up to 100 ml by adding triple distilled water and used to prepare the aqueous supersaturated solution of

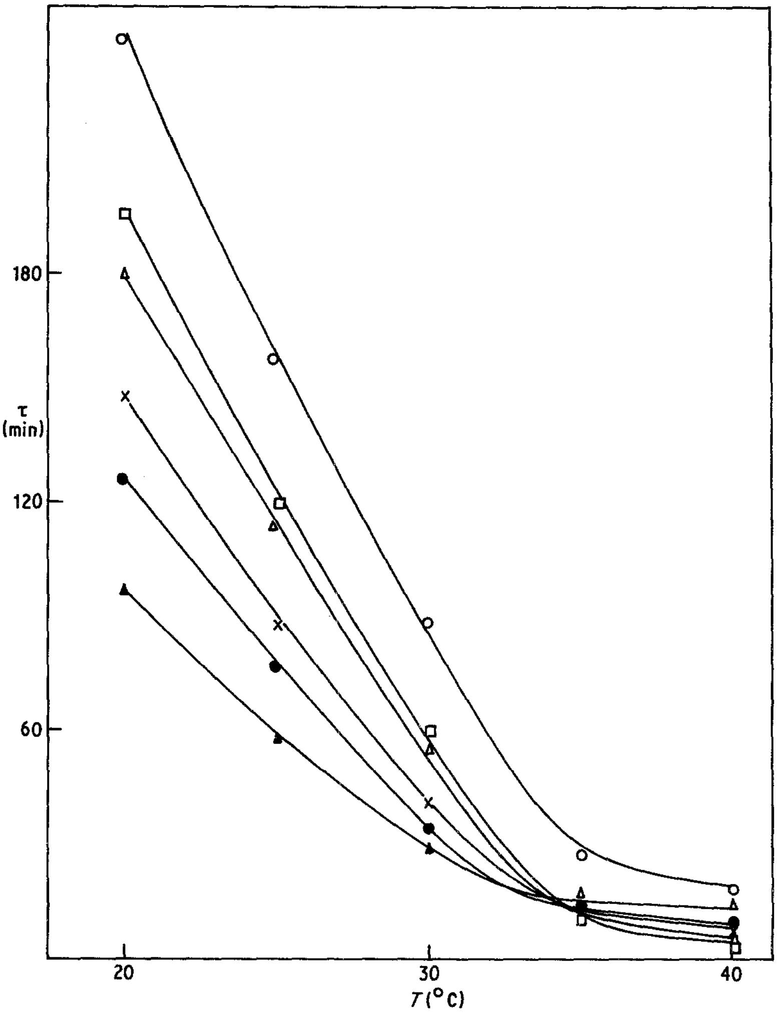

Figure 1 Effect of temperature on induction period (in min) at $S = 1.4$ and impurity concentration = 100 p.p.m. (○ = KDP pure system: □ = K_2CO_3; △ = K_2SO_4; × = $K_2C_2O_4$; ● = $Na_2B_4O_7$ and ▲ = K_2CrO_4).

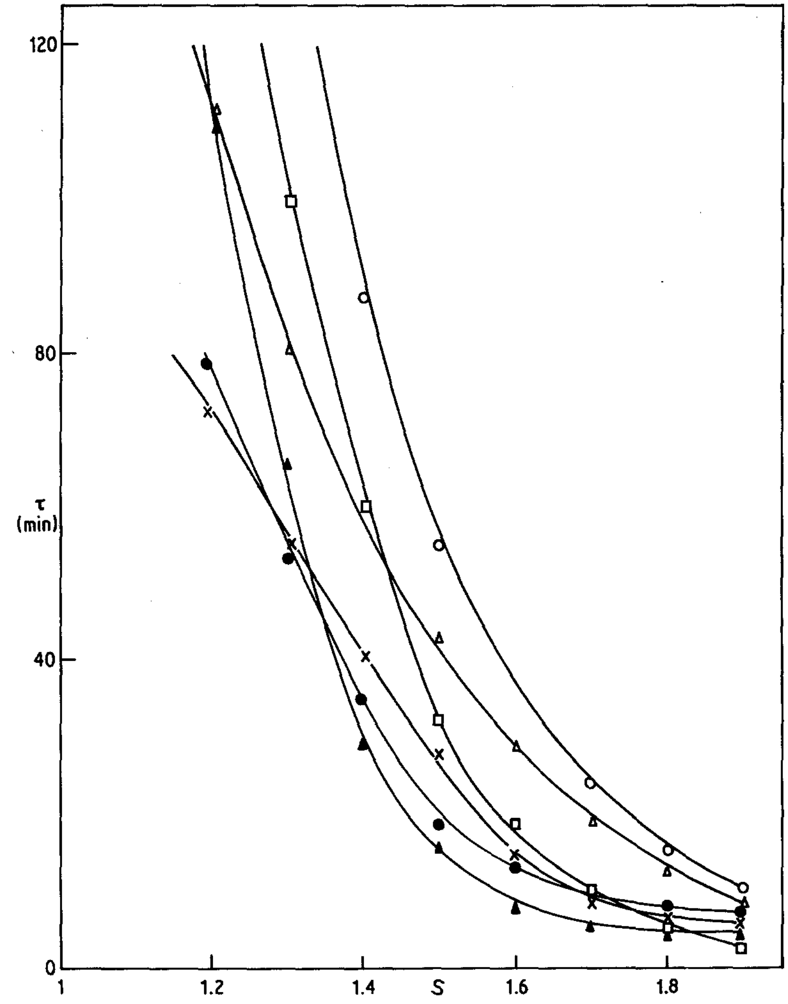

Figure 2 Effect of supersaturation on induction period (in min) at $T = 30°$ C and impurity concentration = 100 p.p.m. (○ = KDP pure system; □ = K_2CO_3; △ = K_2SO_4; × = $K_2C_2O_4$; ● = $Na_2B_4O_7$ and ▲ = K_2CrO_4).

KDP with the added impurity. Experiments are carried out similar to those on the pure system to study the relationship between temperature, supersaturation and induction period of KDP solutions in the presence of soluble impurities. The volume of the solution taken in the nucleation cell is maintained at 10 ml in all the experiments. Experiments are carried out under unstirred conditions.

4. Results

4.1. Effect of temperature

For a particular supersaturation level, experiments are performed at five selected temperatures in the range from 20 to 40° C. The results of such experiments for KDP solutions with and without the presence of the impurities are presented in Fig. 1. It is observed that for a given level of supersaturation, the induction time decreases with increase in temperature.

4.2. Effect of supersaturation

To study the effect of supersaturation on induction period, experiments are conducted for various supersaturations ($S = 1.1$ to 1.9) at a particular temperature. The data presented in Fig. 2 indicate that in all cases the induction period decreases with increase in supersaturation.

4.3. Effect of impurity

The presence of an impurity having a common ion with the crystallizing substance decreases the induction period [26]. Sodium borate (borax) will act as growth aid for the growth of KDP in aqueous solution [27]. For all the divalent anionic impurities considered in the present investigation, it is found that the presence of impurity in the KDP solution reduces the induction time as shown in Figs. 1 and 2.

5. Discussion

The kinetics of nucleation depend on the thermodynamic driving force, which in turn depends on the supersaturation, temperature and impurities present in the system. The induction period, a measure of the nucleation rate, is determined experimentally for KDP solution with and without the presence of impurities at different supersaturations and temperatures. Though experiments are conducted under controlled conditions, crystal nucleation normally occurs earlier than expected, there being less time lag than theory would predict under the conditions. The main reason for this phenomenon is that there are normally between 10^6 and 10^8 impurity particles present per ml of aqueous solution, whatever precautions are taken in performing the experiment. These particles are an aid to heterogeneous nucleation. Considering the principles of homogeneous and heterogeneous nucleation theories, the free energy of formation of a nucleus under heterogeneous nucleation is less than that of a homogeneous condition, as shown by the relation,

$$\Delta G_{\text{heterogeneous}} = \phi \Delta G_{\text{homogeneous}}$$

since $0 < \phi < 1$ in all cases, where ϕ is the shape factor which depends on the shape of the nucleus. For a spherical nucleus

$$\phi = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

where θ is the angle of contact between the nucleus and the substrate.

Fig. 3 shows the plots of $\ln \tau$ against $1/\ln^2(x/x_0)$ drawn with experimental data obtained at 30° C. The plots are not linear at low supersaturation levels. The linear dependence of $\ln \tau$ on the reciprocal of $\ln^2(x/x_0)$ is observed for supersaturations above 1.5. The energy of formation and radius of crystal nucleus depend on the supersaturation level, as shown in Figs. 4 and 5. The values of energy of formation and radius of crystal nucleus at a particular supersaturation $S = 1.5$ are given in Table I. It can be seen from Table I, that the interfacial tension, energy of formation and the critical radius of nucleus are less when the system has added impurities. Similar results are observed in the condensation of water nuclei from vapour in the presence of soluble salts like ammonium sulphate and sodium chloride [28]. Also, the interfacial tension calculated in the present study is less compared to Söhnel *et al.* [29] and Söhnel [30]. Bikerman [31] has reported that the values of σ obtained by other methods differ by as much as several orders of magnitude. Tolman [32] has theoretically proved that the interfacial tension depends on the size of the droplet as,

$$\frac{\sigma}{\sigma_0} = \frac{1}{(1 + 2\delta/r)},$$

where δ is a constant, σ_0 is the interfacial tension when the surface is flat and σ is the interfacial tension for a droplet of radius r. Dufour and Defay [33] have shown that the interfacial tension of water droplet decreases with the decrease in radius of the droplet. Hence the interfacial tension of KDP determined for a macrocrystal will be

TABLE I

Material	KDP pure system	Impurity concentration 100 p.p.m.					Reference
		K_2CO_3	K_2SO_4	$K_2C_2O_4$	K_2CrO_4	$Na_2B_4O_7$	
σ (mJ m^{-2})	5.915	5.809	5.801	5.658	5.498	5.285	Present work
	2.434						[9]
	13						[29]
	15						[30]
ΔG (kJ mol^{-1})	7.647	7.245	7.212	6.693	6.141	5.455	Present work
r (nm)	0.7160	0.7031	0.7022	0.6849	0.6655	0.6397	Present work

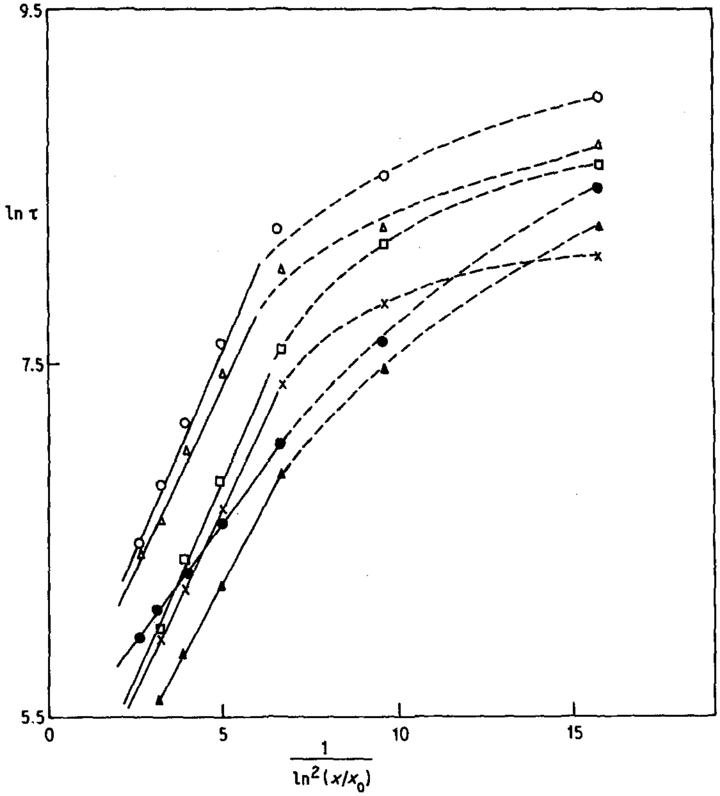

Figure 3 Plot of $\ln \tau$ against $1/\ln^2(x/x_0)$ drawn at $T = 30°$ C with τ in sec, concentration of the impurity = 100 p.p.m. (○ = KDP pure system; □ = K_2CO_3; △ = K_2SO_4; × = $K_2C_2O_4$; ● = $Na_2B_4O_7$ and ▲ = K_2CrO_4).

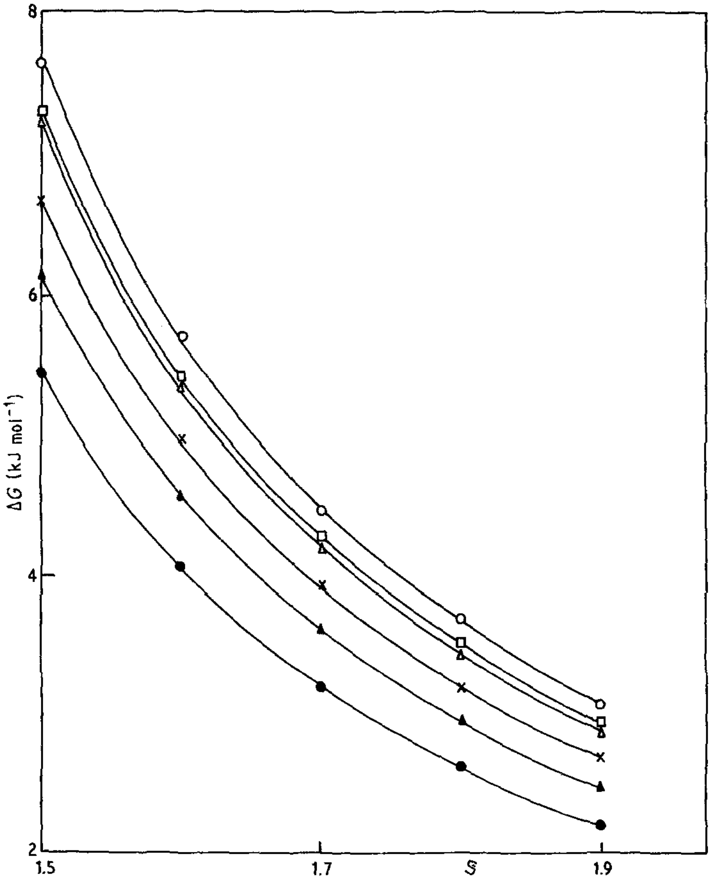

Figure 4 Dependence of energy of formation (kJ mol^{-1}) of crystal nucleus on supersaturation (○ = KDP pure system; □ = K_2CO_3; △ = K_2SO_4; × = $K_2C_2O_4$; ● = $Na_2B_4O_7$ and ▲ = K_2CrO_4).

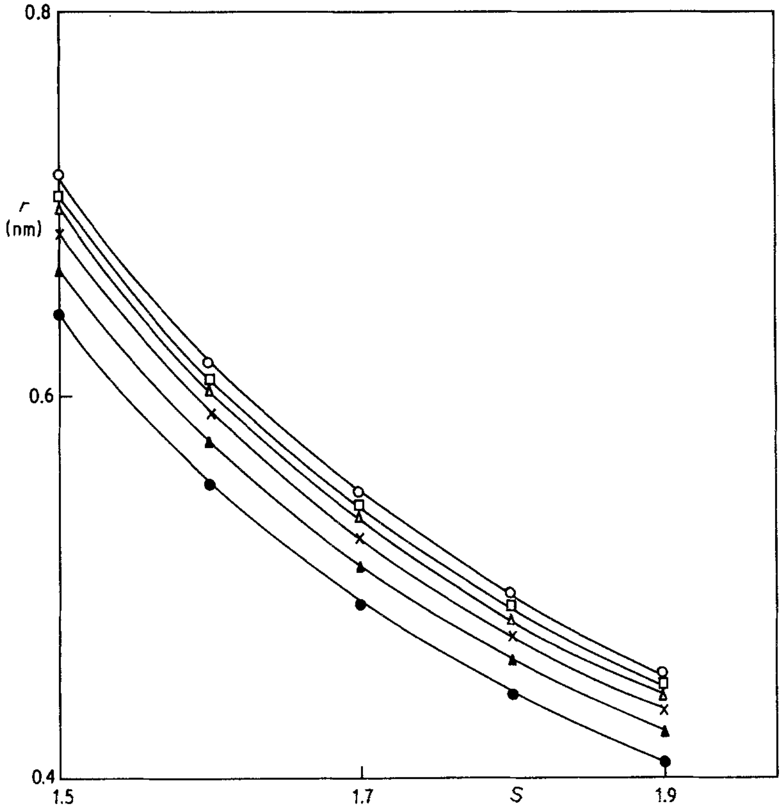

Figure 5 Dependence of radius (nm) of critical nucleus on supersaturation (○ = KDP pure system; □ = K_2CO_3; △ = K_2SO_4; × = $K_2C_2O_4$; ● = $Na_2B_4O_7$ and ▲ = K_2CrO_4).

higher than that of a microcrystal discussed in nucleation experiments.

6. Conclusion

The results of the present study on nucleation in KDP solution with and without the presence of soluble impurities are well explained in terms of classical nucleation theory. The interfacial tension, energy of formation and critical radius of the nucleus are found to decrease in the presence of the impurities considered.

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