TABLE I

POLYMERIZATION OF ISOAMYL VINYL ETHER IN DIETHYL ETHER SOLUTION AT 0°

$[M]_{t=0} = 0.8$ mole l.$^{-1}$, $[I_2]_{t=0} = 0.001$ mole l.$^{-1}$

Pressure, atm.	k sec.$^{-1}$ mole^{-2} l.$^{-2}$	Mol. wt. of polymer
1	5.0	2300 ± 200
500	6.6	
750	9.6	
1000	13.2	2500 ± 200

that these two reactions should be influenced similarly by a change of pressure.[12]

Unfortunately we are unable to decide definitely which step in the polymerization was primarily responsible for the acceleration at high pressures. But it certainly appears that the effect of pressure on the initiating steps

$$2I_2 \longrightarrow I^+ + I_3^- \qquad (2)$$
$$I^+ + M \longrightarrow MI^+ \qquad (3)$$
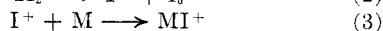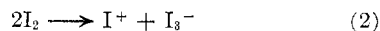
could be sufficient to account for the whole acceleration. Taken together, reactions 2 and 3 are identical with the rate-determining step in the addition of iodine to olefins in solvents of low dielectric constant[13,14]

$$2I_2 + R_2C{=}CR_2 \longrightarrow R_2C{-}\overset{+}{C}R_2 + I_3^- \qquad (4)$$

We have found previously[14] that this reaction is accelerated by a factor of 3.1 at 1000 atm., which is close to the change shown in Table I. The reaction is favored by an increase in pressure because it involves the appearance of electrical charges and a consequent electrostriction of the surrounding solvent.[15,16]

Reactions in Undiluted Monomer.—In these experiments the iodine reacted completely and almost instantaneously with the monomer to form a colorless complex, or addition compound, having an absorption band at 280 mμ. This was presumably the "inactive complex"

$$\begin{array}{c} CH_2 \\ \parallel \ \longleftarrow I_2 \\ RO{-}CH \end{array}$$
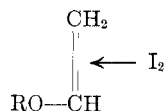
discussed by Eley and Saunders.[8] However we found that the complex was active as a catalyst, and that the vinyl ether proceeded to polymerize slowly according to the rate equation

$$-\frac{1}{[M]}\frac{d[M]}{dt} = k\,[MI_2], \ ([M] \gg [MI_2]) \quad (5)$$

where $[MI_2]$ denotes the concentration of the iodine complex. In contrast to the polymerization in diethyl ether solution, this reaction was well behaved under pressure and we were able to make measurements to 10,000 atm. without complications. Our results are given in Table II.

(12) It is significant that Eley and Saunders[8] have found that although a change in the structure of the vinyl ether may have a large effect on the *rate* of polymerization, it has only a small effect on the *degree* of polymerization.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 666.

(14) S. D. Hamann and D. R. Teplitzky, *Disc. Faraday Soc.*, **22**, 114 (1956).

(15) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).

(16) Reference 2, p. 164, *et seq.*

TABLE II

POLYMERIZATION OF PURE ISOAMYL VINYL ETHER AT 0°[a]

$[MI_2] = 0.001$ mole l.$^{-1}$

Pressure, atm.	$10^3 k$ sec.$^{-1}$ mole^{-1} l.
1	1.5
1,000	4.5
2,000	7.8
3,000	11.0
10,000	40

[a] The molecular weight of the polymer was not determined.

We can explain the change of reaction order with respect to the total amount of iodine (equations 1 and 5) in the following way. In diethyl ether solution the initiating step (2) requires the presence of two I_2 molecules and for this reason the rate of polymerization is of the second order in $[I_2]$. But, in the undiluted monomer, the absence of any free iodine rules out the possibility of reaction 2 and we suggest that instead the initiation occurs through breakdown of the addition complex as

$$MI_2 + M \longrightarrow MI^+ + MI^- \qquad (6)$$
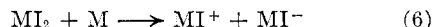
This mechanism implies that, in the presence of a large excess of monomer, iodide ions can form complexes with the monomer in the same way as they do with iodine. This is a reasonable supposition since it is known that iodide ions form strong complexes with other olefinic compounds such as maleic anhydride.[17] Initiation by reaction 6 would lead to over-all kinetics of the first order in $[MI_2]$.

It is likely that reaction 6 proceeds through a transition state in which the initial I–I bond is partially ionized. It is closely analogous to reaction 2 and it should be similarly accelerated by pressure. We can therefore conclude, again, that the increase in rate of the initiating step *could* account for the whole of the influence of pressure on the polymerization. But on the present evidence we are unable to be sure that it is the only factor involved.

(17) E. M. Kosower, R. L. Martin and V. W. Meloche, *J. Chem. Phys.*, **26**, 1353 (1957).

CRYSTALLIZATION ON A SEED FROM FUSED SALT SOLUTIONS BY THE TEMPERATURE DIFFERENCE METHOD

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Recently considerable success has been obtained in the growth of single crystals of refractory oxides and other water-insoluble materials from fused salt solutions. With a little perseverance, one can usually find a salt or combination of salts which will dissolve, reversibly, in the molten state, considerable quantities of the material to be crystallized. The main criterion for success is that the crystal desired exists as the stable solid phase at the temperatures and compositions of molten solution employed.
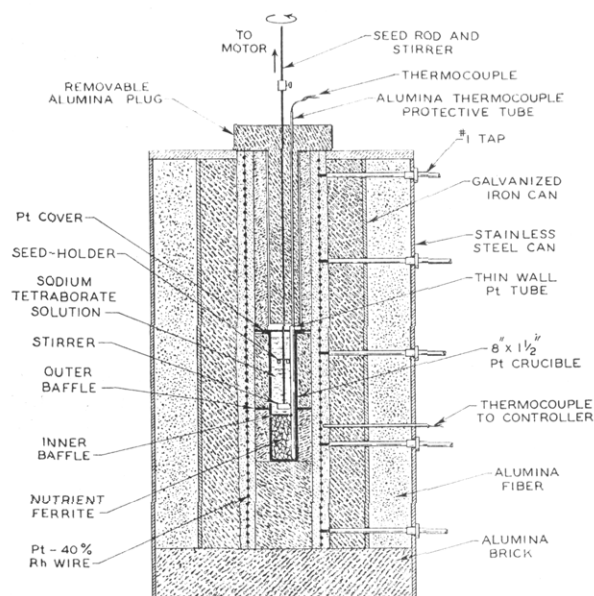
Fig. 1.

Analogous to crystal growth from aqueous solutions, there are three major methods by which single crystals can be grown from fused salt solutions. These are: (1) growth by the slow cooling of a saturated solution; (2) growth by the evaporation of the solvent phase and (3) growth by the temperature difference method, sometimes known as the Krüger–Fincke principle.[1]

Examples of the application of the first method to fused salt solutions are the growth of single crystals of barium titanate from molten potassium fluoride[2] and magnetic garnets from molten lead oxide.[3] The second method occasionally has been employed,[4] but it is handicapped by the difficulty in obtaining controlled evaporation and the high temperatures required. The third method, growth by a temperature difference between a nutrient zone and a crystallization zone, has not previously been exploited for growth from fused salt solutions; and it is the purpose of this note to present the results of a preliminary investigation of the extension of this method to fused salt systems.

The procedure as outlined in the experimental section describes the growth of cobalt ferrite from molten sodium tetraborate as an example of the application of the temperature difference method to fused salt solutions. This method also has been used with some success for growing calcium fluoride from a lithium chloride–potassium chloride eutectic mixture.

Experimental

Figure 1 shows the details of the apparatus used in these experiments. Since the control of temperature differential and fluctuation were believed to be most important to the controlled growth of crystalline material on a seed from a fused salt solution, care was taken in the design and con-

struction of the furnace equipment. Some features of the furnace are as follows: (1) High temperature alumina brick and alumina fiber were used as insulation, and all the space around the crucible inside the furnace was filled with insulation to give a larger thermal mass. (2) Many taps leading from the furnace winding were made available in order to vary the voltage distribution over the length of the furnace to give flexibility in adjusting the temperature differential. (3) Platinum baffles were fixed inside and outside of the crucible to effect a sharp thermal gradient between the nutrient chamber and the crystallization chamber. (4) A thin wall platinum tube attached to the inside wall of the crucible made it possible to telescope a thermocouple, up or down, to record temperatures at different levels in the molten solution. (5) The platinum rod used for holding the seed was extended out of the furnace and attached to a motor for stirring the solution and rotating the seed. (6) A tightly fitting platinum cover on the crucible made the loss of material by vaporization negligible. (7) A saturable core reactor temperature controller was employed to give a stepless temperature control.

The procedure followed in obtaining growth on a cobalt ferrite ($CoFe_2O_4$) seed by the temperature difference method was as follows.

The $CoFe_2O_4$ which was used for nutrient and seed material was prepared by crystallizing sintered $CoFe_2O_4$ from a slowly cooled PbO solution.[5] These crystals were unusually large, but badly flawed by cracks and solvent inclusions. The sodium tetraborate (borax) which was used as the solvent in most of the experiments was prepared by heating sodium metaborate with boric anhydride. The solution was prepared by mixing $CoFe_2O_4$ sintered powder with borax and heating to 1100° for 48 hours. The molten liquid was then decanted into an iron dish leaving behind the undissolved $CoFe_2O_4$. This procedure ensured a solution very near the saturation point.

The bottom two inches of the platinum crucible were filled with crystalline $CoFe_2O_4$. The baffle and thermocouple protection tube were put in place and the crucible was filled with chunks of the saturated solid solution of ferrite in borax. The crucible was lowered into the furnace and the temperature slowly raised until all the solid solution was molten. Additional chunks were added until the charge was full. When all of the material above the baffle was liquid, the stirring apparatus without the seed was lowered into the solution and the furnace plug put into place in order to make accurate temperature measurements. The temperature above the baffle was raised to 1120°. After 24 hours under these conditions, the temperature was lowered 30° in order to supersaturate the solution. The stirring apparatus then was withdrawn and a small seed attached. After preheating, the seed was lowered into the solution and stirring begun. From time to time the seed was withdrawn for inspection, and the amount of growth noted.

Results and Discussion

Employing growth times of 2 to 20 hours, temperature differences of 10 to 50°, and crystallization temperatures of 1100 to 1200°, one obtains growth rates averaging 5 weight % increase per hour. These crystals were grown to twice the original seed size and measured 1 to 1.5 cm. in the largest dimension. The growth occurred by means of terraces parallel to the 111 octahedron faces. In several runs it was noted that when spontaneous nucleation produced crystals on the stirring rod above the seed, these crystals developed into regular octahedra with smooth 111 faces. This would lead one to infer that the imperfections (both stoichiometric and crystallographic) in the crystal seed caused the irregular growth features.

Although the temperature difference method has several intrinsic advantages, and has worked admirably for growth from aqueous solutions[6] and for hydrothermal crystal growth,[7] its application

(1) F. Krüger and W. Fincke, German Patent 228,246, Kl. 120, Gr. 2. Nov. 5, 1910.

(2) J. P. Remeika, *J. Am. Chem. Soc.*, **76**, 940 (1954).

(3) J. W. Nielsen and E. F. Dearborn, *Phys. Chem. Solids*, **5**, 202 (1958).

(4) V. A. Timofeeva and A. V. Zalesskii, *Rost Kristallov*, **2**, 88 (1958).

(5) J. P. Remeika, *J. Am. Chem. Soc.*, **78**, 4259 (1956).

to fused salt solutions presents a number of difficulties.

It was found that even though the "average" temperature of the growing chamber could be held almost constant, still hot currents existed which would cause a crystal seed to dissolve at one position in the crystallization zone while at the same time to grow in another. For this reason, an apparatus was designed for the rotating of the seed concurrently with the stirring of the solution in order to dissipate these hot currents.

Further, it is difficult to obtain a sharp temperature gradient between the nutrient and crystallization chambers in the vertical furnace employed in this work with but a single inner baffle because of the efficient heat conduction of the platinum crucible containing the fused salt solutions. However, it was found that by employing an outer baffle of platinum around the cylindrical crucible to reflect the furnace heat downward, together with a properly positioned inner baffle, a fairly sharp temperature gradient of up to 80° could be obtained.

Once these difficulties are overcome the temperature difference method should be capable of yielding crystals of high perfection. This is because the crystal is grown under isothermal conditions and, hence, should have a minimum of thermal strains, and also because by controlling the magnitude of the temperature difference, the crystals can be grown at any desired constant supersaturation. If the stoichiometry of the crystals can be used as a measure of their perfection, then the $CoFe_2O_4$ crystals grown as described above are superior to the $CoFe_2O_4$ crystals previously grown by the slow cooling of molten solutions of PbO_2. They have a Co to Fe ratio of 0.50, whereas the aforementioned crystals gave a Co to Fe ratio of anywhere from 0.56 to 0.67,[8] as determined by direct analysis.

Work is now in progress to grow larger crystals using longer growth times, and to increase crystal perfection and minimize spontaneous nucleation by finding optimum conditions of supersaturation and temperature. Also, this investigation is being extended to other crystals and other fused salt solvent systems.

(6) A. C. Walker and G. T. Kohman, Bell Telephone System, Tech. Pub., Monograph B-1562; also, Trans. Am. Inst. Elec. Engrs., 67, 565 (1948).

(7) R. A. Laudise and J. W. Nielsen, "Hydrothermal Crystallization, Solid State Physics," Academic Press, New York, N. Y., in press.

(8) J. W. Nielsen, private communication.

SPIN-SPIN COUPLING CONSTANTS BETWEEN NON-BONDED C^{13} AND PROTON.

II.[1] DEPENDENCE OF $J_{C^{13}-C-H}$ ON HYBRIDIZATION OF C^{13}

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Theoretical and experimental studies on n.m.r. interactions between non-bonded H–H, H–F and

(1) Part I, G. J. Karabatsos, J. Am. Chem. Soc., 83, 1230 (1961).

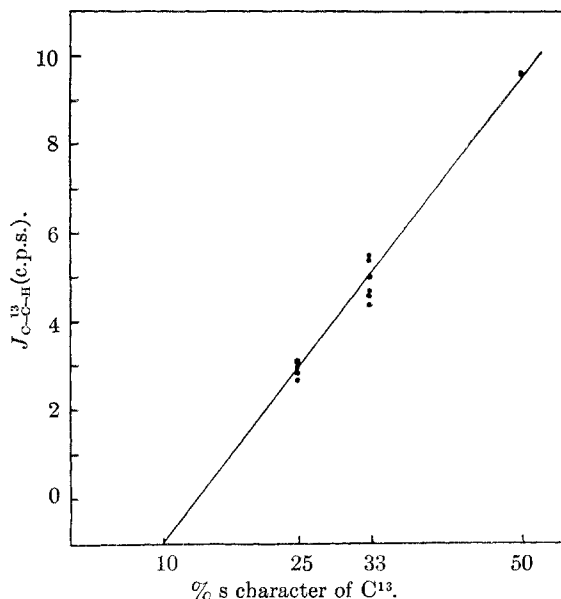% s character of C^{13}.

Fig. 1.

F–F have been carried out and published, while analogous studies involving non-bonded C^{13} and protons have not been made.[1] We wish to report here some of our findings involving C^{13} and protons separated by one carbon atom.

The spin-spin coupling constants $(J_{C^{13}-C-H})$ for eleven compounds were measured and the results are summarized in Table I. The enrichment in the samples varied from 30 to 60% excess C^{13}. All spectra were taken with a model V-4300D Varian Associates Spectrometer, at 60 Mc.; spin-spin coupling constants were measured by the standard side band technique.[2]

The data fall into three categories: (1) When the C^{13} is sp^3 hybridized $J_{C^{13}-C-H}$ has an average value of about 4.0 c.p.s. (2) When the C^{13} is sp^2 hybridized the average value of $J_{C^{13}-C-H}$ is about 5.9 c.p.s. (3) When the hybridization of C^{13} is sp the value of $J_{C^{13}-C-H}$ is about 10.6 c.p.s. (only one value available).

It has been shown[3] that for protons directly bonded to C^{13} a linear correlation exists between the magnitude of $J_{C^{13}-H}$ and the extent of sp hybridization of the carbon atomic orbitals. The data presented in Table I show that this correlation is a general one and can be applied to interactions between C^{13} and protons separated by two bonds. If a plot of $J_{C^{13}-C-H}$ vs. % s character of C^{13} atomic orbitals is made, a linear relationship is obtained (Fig. 1). However, while no appreciable intercept is found[3a] in the case of $J_{C^{13}-H}$, an intercept in the case of $J_{C^{13}-C-H}$ is evident. In order to assess the importance of the Fermi contact term theoretical calculations were performed, using the procedure of Gutowsky and Karplus.[4] The following assumptions were

(2) J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 1608 (1951).

(3) (a) J. N. Shoolery, ibid., 31, 1427 (1959); (b) N. Muller and D. E. Pritchard, ibid., 31, 768, 1471 (1959).

(4) H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).