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*J.W. Hackett, Jr.*



Published by  
The Phi Chi Club of  
PROVIDENCE COLLEGE  
Providence, R. I.

J. Joseph Hanley

Twenty-five years of Service  
to Providence College

# *The* Entropy

# THE ENTROPY

Formerly The Providence College  
Journal of Physics and Chemistry

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Keeping pace with the general advancement and expansion of Providence College, the Chemistry Department has, this year, initiated a program of graduate study leading to the degree of Master of Science. Attractive teaching assistantships are available and basic courses and specialized research undertaken in all major branches of Chemistry.

This program brings qualified, capable instructors to the laboratory and enables the professor to undertake more fruitful endeavors.

D. J. K.

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## ON THE COVER

Mr. J. Joseph Hanley, associate professor of chemistry and senior lay member of the Providence College faculty will complete twenty-five years of teaching here this June.

Mr. Hanley received his undergraduate and graduate training at P. C., taking the Ph.B. degree in 1931, and the M.S. degree in 1936. His graduate thesis, under the direction of Dr. John A. McGrail, was entitled "Study of the Reactions of the Carbonyl Group."

An instructor of chemistry in 1931, Mr. Hanley was made assistant professor in 1936 and associate professor in 1947. During the early war years (1942-3) his research with Father Hickey resulted in the publication of several papers on war gases, their preparation and detection, with special reference to civil defense applications. He was consulting chemist in a plastic coating research project in 1943. He also collaborated with Fr. Hackett and Dr. Fineman on the Office of Naval Research sponsored study of electrochemical properties of anodic materials. Our jubilarian is a member of the New England Association of Chemistry Teachers and the American Chemical Society, being A. C. S. Rhode Island Section vice-chairman (1951-3) and chairman (1953-5). He is now serving on the Executive Committee. Mr. Hanley presently teaches qualitative organic analysis and general organic chemistry. In the past he has conducted courses in theoretical organic as well as general and inorganic analytical chemistry.

Faculty members know Mr. Hanley as a loyal and devoted fellow teacher with a fine spirit and one easy to work with. Students know "Uncle Joe" as an inspiring lecturer always ready to give aid and counsel, whether professional or personal. Though he might be characterized by many as "the man with the big cigar and kindly acrid wit," he is also known for his "unknowns" of distilled water, lachrymators and thioglycollic acid derivatives (familiar to many).

Tribute to this fine man cannot be excessive. THE ENTROPY offers its sincerest congratulations to Mr. Hanley on this silver anniversary and wishes him many years of continued success at Providence College.

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"We'll get our Research Department on that right away, sir!"

— Courtesy CHEMICAL PROCESSING



## NYLON 6,6<sup>1</sup>

Charles E. Crepeau, B. S. '55

Nylon is a generic term for any long chain synthetic polyamide which is capable of being formed into a filament, the structural elements of which are oriented in the direction of the fiber axis.

Early work leading to the discovery of high molecular weight synthetic polyamides was done by W. H. Carothers in 1930. He studied the poly-condensation of difunctional molecules from which linear polymers were produced. The initial reactions investigated were between selected dibasic acids and glycols. The polyesters produced had molecular weights in the range of 2300 to 5000 and had relatively low melting points.

The preparation of still higher molecular weight compounds (10,000 or above) was facilitated by the use of a modified molecular still. The term superpolymer was applied to these materials. It was observed that these superpolymeric substances could be drawn into filaments, and this sustained the hope that it might be possible to make a fiber of commercial value from such a substance. After much research, polyamide formation from aminononanoic acid was selected for further study. This poly-

amide was found to melt at 195°C. and, after spinning and cold drawing, it produced fibers which were equal to natural silk in strength and pliability. Numerous other polyamides were then synthesized from various combinations of amino acids, dibasic acids and diamines. The most promising of these was the superpolymer, hexamethylene adipamide, which is more commonly known as nylon "6,6", the first 6 indicating the number of carbon atoms in the dibasic acid.

Commercially, nylon is prepared by reacting hexamethylene diamine and adipic acids to form hexamethylene diammonium adipate, or nylon salt. The solution is then decolorized with activated carbon and adjusted to the proper pH and concentration prior to polymerization.

In principle, the conversion of nylon salt to polymer involves heating it to a temperature at which condensation of the amine and carboxyl groups occurs, thereby forming amide linkages and releasing water. In practice, this involves heating the solution in an autoclave to prevent the escape of the amine component of the salt with the steam released during heating and provide accurate control of the extent of polymerization throughout the batch. The closed autoclave is heated until the pressure reaches 250 p.s.i. At this point steam is slowly bled off in order to maintain constant pressure. During this period sufficient condensation of the salt occurs to fix the originally volatile amine by partial polymerization. Furthermore, by operating at this pressure, the boiling point of the batch is sufficiently high to prevent the precipitation of a solid polymer phase. When

<sup>1</sup> Edited from a seminar given March 18, 1954.

a temperature of 275°C. is reached, the pressure is allowed to fall slowly until atmospheric pressure is reached. The rate of cooling is regulated so that freezing of the batch is prevented. The product can then be spun directly or solidified into flakes, for shipping to other spinning plants.

The next step, cold-drawing, is the backbone of the process because it produces a very desirable molecular change. This consists of a gradual rearrangement of the polymer molecules from a random distribution to a highly oriented one. The long chains are aligned side by side and brought very close together by inter-molecular linkage, resulting in an increase in the tensile strength of the fiber. By varying the draw ratio, it is possible to prepare from a single polymer species a family of fibers which have different, individual tensile strengths.

The chemical and physical properties of nylon after cold-drawing are attributed to the molecular arrangement which can be represented by the following formula:

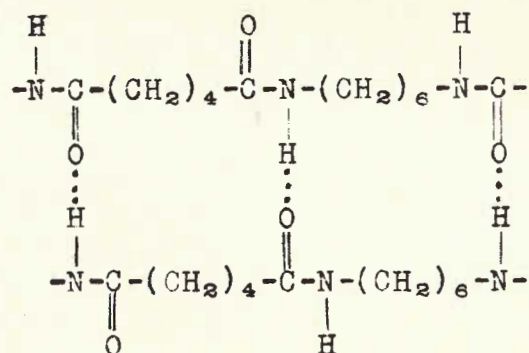


Figure 1. Section of nylon fiber.

It can be seen that the amide groups are positioned in such a way as to exhibit hydrogen bonding in both directions. If the number of methylene groups is small and there are no bulky side groups attached to the molecular chain, there results a tough, strong, high melting fiber. This occurs because the many points of inter-molecular attraction tie the polymer units together into complexes similar to macro-molecules. This close packing of molecules is probably the main difference between nylon and natural fibers. All natural fibers are loosely packed and consequently hydrophilic. When water molecules are entrapped between the molecules of a natural fiber they evaporate and leave the fiber in a crimped or shrunken form. Nylon is closely packed and hydrophobic; the fiber shows no appreciable shrinkage under normal conditions.

The structure of nylon is also the basis for its chemical properties. The nylon molecule has only two types of groups: the methylene and the amide. The chain of methylene groups is relatively unreactive, and so the fiber is tough and relatively stable to chemical attack. The amide groups are the only active points in the molecule. These are tied up by inter-molecular bonds and therefore are subject only to strong hydrolytic forces. Molds, micro-organisms and insects have no effect on pure nylon. Certain dyes or coating material however, will entice some few species of insects to eat nylon.



The chemical inertness of nylon and its unique physical properties suggest many applications. Its toughness, elasticity and light weight make it ideal for hosiery, fishing leaders and lines, baseball winding, etc. Because of its high resistance to abrasion and its relative inertness, it has also been used to make tow ropes, brushes, filters and surgical sutures. The number and diversity of applications of Nylon 6,6 is constantly increasing.

#### References:

1. Quig, J. B. and Dennison, R. W. "Functional Properties of Synthetics" Ind. and Eng. Chem. 44, 2176 (1952).
2. Quig, J. B. "Technical Developments Leading to Man-Made Fibers" Textile Research Journal 23, No. 5 (1953).
3. "Encyclopedia of Chemical Technology" 10, 916-934.

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#### VISIBILITY ZERO

A speaker should still consider,  
When he's preparing that slide,  
Has he got something he wants to show  
Or something he's trying to hide.

Courtesy C. and E. News

#### PRINTED CIRCUITS<sup>1</sup>

Leo D. Cotter, B. S. '55

An improvement in radio receivers of today is the use of printed circuits. Considered to be one of the major electronic developments of World War II, printed circuits have miniaturized condensers and resistors.

A rapid and economical method of making electrical circuits employs a copper etching process which was borrowed from the radio industry. This photo-engraving method makes it possible to mass-produce miniature electronic package assemblies.

Essentially, three preliminary steps bring an electronic unit close to the final assembly:

The first step consists in the photographing of an engineer's drawing of the circuit. The negative used is made of a stiff vinylite-base film which is not subject to distortion. The circuit then appears on the black negative as transparent lines the exact size and shape of the circuit.

The second step involves the transfer of the image to a copper plate, bonded on one side to a piece of phenolic electrical insulation board. The board is about one sixteenth inch thick,

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<sup>1</sup> Edited from a seminar given April 23, 1954.

and the copper veneer is about three-sixteenths inch thick. The copper plate is then coated with a light sensitive engraver's enamel: cold top. Then the plate is whirled while it is exposed to ruby infrared light, thus spreading the enamel evenly and drying it at the same time. The negative is placed over the plate, and the two are held in close contact in a vacuum printing frame. A 95-amp arc light throws a glaring blue light on the negative. The enamel exposed through the transparent lines of the wiring diagram is thus hardened. Finally, the copper plate is put into a developing solution which washes away the unhardened portions of the enamel. The lines of hardened enamel which remain on the copper plate constitute the wiring diagram.

The final step is accomplished by placing the plate in an etching tank containing a ferric chloride solution to dissolve the copper. That portion of the copper plate protected by the enamel lines is preserved, while the balance of the copper plate is dissolved. This leaves the wiring circuit in copper on the phenolic board. Two to four minutes are required for each phase of the process described.

The phenolic board is sent to the factory where holes are drilled as required. Electronic devices, such as miniature radio tubes, condensers, and resistors, are fastened to the back of the board. Pins from these devices go through the drilled holes and contact the copper wiring circuit on the other

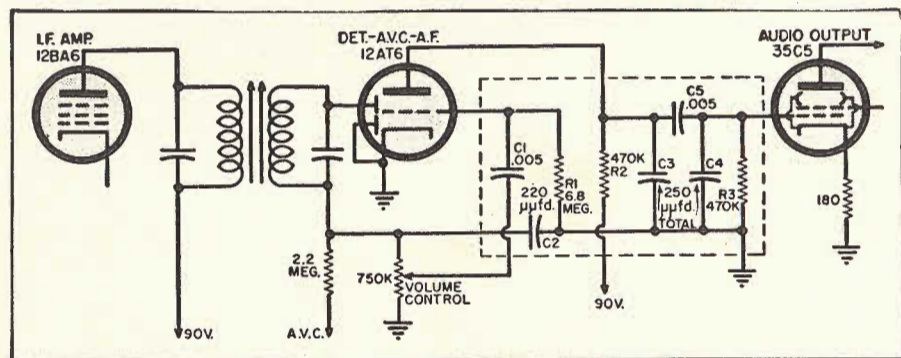
side. The entire circuit is then floated in a solder bath, circuit side down. All the connections are soldered at once, and the complex assembly is completed in less time than the wiring of many single circuits.

Another process for printing circuits starts with a plain piece of bakelite which has been punched or drilled to receive non-printed components of the complete circuit. Those places where no circuitry is desired are screened with a paint or ink. The unpainted portions of the bakelite are then plated with a layer of copper one to three millimeters thick. The copper plating is continuous through the bores of all holes or punched sections, as well as the opposite side and all edges. In other words, eyelets are plated right through the holes. This is important since it allows connection from one side of the bakelite chassis to the other without using external leads. It is evident that no metal is wasted, and only the actual amount needed for the printed circuit is used. This method also has the advantage of using the same soldering process to connect added components to the printed wiring. The printed circuit may then be treated with a protected coating, encapsulated or otherwise packaged, depending on its ultimate application.

The chief application of the printed circuit in radio sets has been in the network between the diode detector and the grid of the audio amplifier as shown

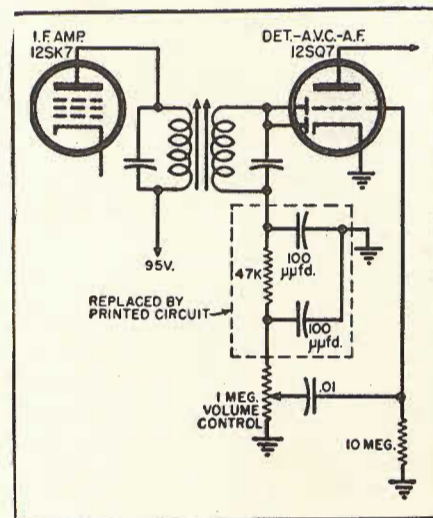


in Figure 1. Here the area within the dotted lines is replaced by a printed circuit. The circuits are available with a variety of condenser and resistor values and with a number of components. For example, one of the simplest printed circuits in use contains the two bypass condensers and series resistor in the load circuit of the diode detector.



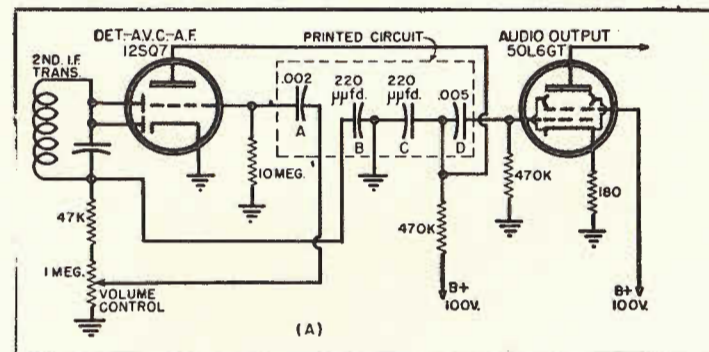
**Figure 1.** In this partial schematic, a single printed circuit unit replaces five condensers, and three resistors in the audio amplifier stages of a set.

Figure 2 shows the printed circuit with three leads extending from it. One goes to the ground, and the other two are connected between the volume control and the bottom of the secondary winding of the i.f. transformer. The circuit is symmetrical, and once the ground wire is established, either one of the two remaining wires may be connected to the volume control and the other to the i.f. transformer.



**Figure 2.** Partial diagram of an AM receiver showing the components that can be replaced by a printed circuit.

There is no limit to the complexity of these printed circuits, and they may contain as many condensers and resistors as any particular application requires. Thus, in Figure 3 the printed circuit contains four condensers ranging in value from 22 μfd. to 0.005 μfd. in a non-symmetric unit provided with six leads.



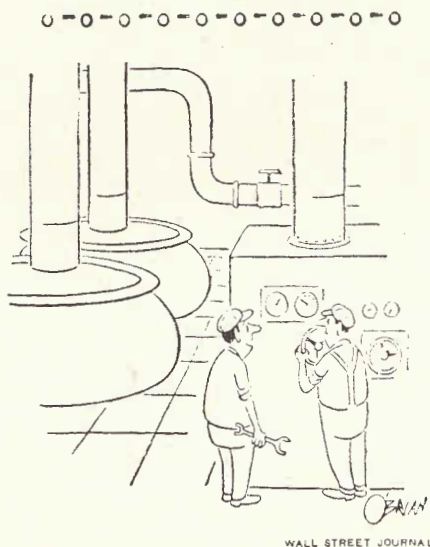
**Figure 3.** Printed circuit consisting of four condensers, as used in an AM receiver.

A most amazing printed circuit is a complete three stage sub-miniature speech amplifier. It is built on a thin light-weight ceramic plate and is about the size of a postage stamp.

There are many other configurations that these printed circuits may assume, but those discussed are representative.

#### References:

1. Lanzollotti, S. J., and Bassler, S. G., Radio and Television News, 48, 13 (1952).
2. Information Bulletin No. 102, Squier Signal Laboratory, Fort Monmouth, New Jersey (1954).
3. Kay, M. S., Radio and Television News, 51, 50 (1954).



I'm new here. What are we making?

#### FELLOWSHIP WINNER



JOSEPH J. SYZMANSKI

Previous Providence College winners of National Science Foundation Fellowships are joined this year by Joseph J. Syzmanski, a June graduate in physics.

N. S. F. competition is open to any United States citizen who has demonstrated ability and special aptitude for advanced training in sciences. The selection of first year fellows is based on academic records and recommendations regarding the candidate's abilities and his score on the Graduate Record Examinations

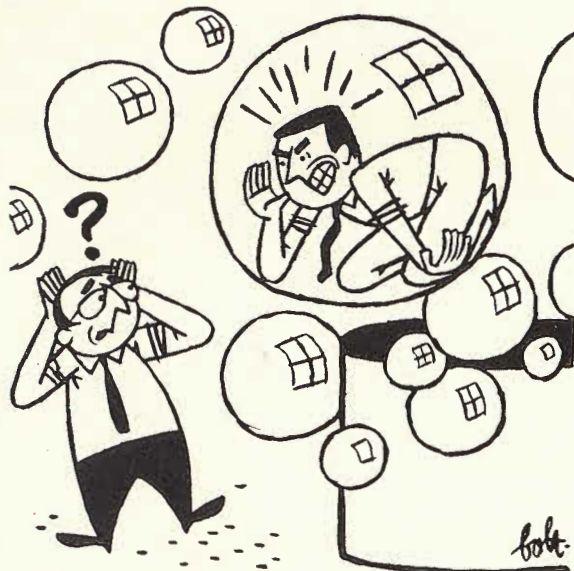


in his chosen field. The award carries an annual stipend of \$1400 plus tuition and fees to the graduate school of the winner's choice whether here or abroad.

A native of Providence and graduate of LaSalle Academy, Mr. Syzmanski will pursue advanced studies in theoretical physics at Harvard University. He has placed high on the Dean's Honor List during his entire career at P. C. and will be class salutorian.

Other applicants from Providence College for the awards given honorable mention by the Foundation are: Joseph Robertshaw, physics; Robert Bento, physics; and David Karl, chemistry. George F. Martins '55, chemistry, was a fellowship winner last year.

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"Don't just stand there! Get the foam killer!"

— Courtesy CHEMICAL PROCESSING

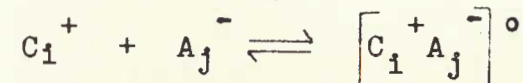
## BJERRUM'S THEORY OF ION-PAIRS<sup>1</sup>

David J. Karl, '56

The modern treatment of solutions of electrolytes had its beginnings in 1887 with the electrolytic dissociation theory of Arrhenius, the fundamental assumption of which is that all electrolytes are partially ionized.

A major modification of this theory was made in 1923 by Debye and Hückel who stated that due to electrostatic attraction in solutions of strong electrolytes ionic interaction takes place. The fundamental idea underlying their deductions is that of ionic atmospheres. Due to Coulomb forces, each ion is surrounded in its immediate neighborhood by an excess of ions of opposite charge.

An extension of the Debye-Hückel Theory was considered by Bjerrum in 1926 to eliminate the difficulties in solving the extended Debye-Hückel equation of LaMer and Sandved. This theory develops from a consideration of the factors which determine the extent of ion-pair formation of the type:



Thus while ionization may be complete dissociation is incomplete. The basic

<sup>1</sup> Edited from a seminar given April 18, 1955.

assumptions made are: that the ions are rigid unpolarizable spheres of radius  $a$ ; in a medium of fixed macroscopic dielectric constant; no non-polar quantum bonds form; and no solvent-ion interaction takes place.

The probability,  $w$ , that an  $i$ -ion is at a distance  $r$  from a  $j$ -ion of opposite charge is given according to the Maxwell-Boltzmann distribution law by

$$(1) \quad w = n_i e^{u/kT}$$

where  $n_i$  is the number of  $i$ -ions with potential energy  $u$  at absolute temperature  $T$ , and  $k$  is the Boltzmann constant. If the ionic atmosphere is pictured as a spherical shell of radius  $r$  and thickness  $dr$  circumscribing the  $i$ -ion, the probability becomes

$$(2) \quad w = n_i e^{u/kT} (4\pi r^2 dr).$$

Within the region where Coulombs' Law is valid, the potential energy or work done in separating an  $i$  and  $j$ -ion from  $r$  to  $\infty$  is

$$(3) \quad u = \frac{Z_i Z_j e^2}{Dr}$$

where  $Z_i$  and  $Z_j$  are the valences of the ions,  $e$  is the charge of the electron and  $D$  the macroscopic dielectric constant of the medium.

Combining equations (2) and (3), the probability function becomes

$$(4) \quad w = n_i \left( \exp \frac{Z_i Z_j e^2}{DrkT} \right) 4\pi r^2 dr.$$

When the ions are of opposite charge,  $w$  possesses a minimum value

$$(5) \quad r \text{ (min. prob.)} = q = \frac{e^2 |Z_i Z_j|}{2DkT}$$

Bjerrum assumed two ions at a distance  $r < q$  to be associated. For 1:1 electrolytes in a medium of high dielectric constant such as water and at 25°C,  $q = 3.51 \text{ \AA}$ . Consequently ions having a minimum distance of approach,  $a_0$ , (i.e., the distance between the centers of the two ions in the ion-pair) less than  $3.51 \text{ \AA}$  will form short range ion-pairs. When  $a_0$  is larger than  $q$ , Coulomb forces are no longer strong enough to hold the ion-pair together and their interaction can be adequately described by the atmosphere theory of Debye and Hückel.

The degree of association for the ion-pair  $(1 - \alpha)$ , where  $\alpha$  is the degree of dissociation, will be given by the definite integral

$$(6) \quad (1 - \alpha) = 4\pi n_i \int_{a_0}^q \exp \left[ \frac{|Z_i Z_j| e^2}{DrkT} \right] r^2 dr$$

Through appropriate substitutions this equation may be expressed as

$$(7) \quad (1 - \alpha) = 4\pi n_i (a_0 b)^3 Q(b)$$

where  $Q(b)$  is a function of  $b$ , and  $b$  has the value

$$(8) \quad b = \frac{|Z_i Z_j| e^2}{a_0 DkT}$$



The equilibrium constant for the formation of the ion pair ( $K^{-1}$ ) is given by

$$(9) \quad K^{-1} = \frac{1 - \alpha}{C}$$

where  $C$  is the molar concentration. This simplified expression may be used since as  $C$  approaches zero both the activity coefficients and  $\alpha$  approach unity. Substitution of equation (7) into equation (9), remembering that  $n_1 = NC_1/1000$  ( $N$  = Avogadro's number) yields

$$(10) \quad K^{-1} = \frac{4\pi N}{1000} (a_0 b)^3 Q(b).$$

Since values of  $Q(b)$  have been calculated from  $D$  equal to 2 to 80, the equilibrium constant for the ion-pair can be evaluated.

The theory of Bjerrum has been verified by Fuoss and Kraus through conductance data of tetraisoamylammonium nitrate in dioxane-water mixtures. Equivalent conductances were determined for solutions in which the dielectric constant was varied from 2.1 to about 45 debyes and concentrations of  $8 \times 10^{-3}M$  to  $8 \times 10^{-4}M$ .  $K$ 's were calculated from Onsager's approximate equation:

$$(11) \quad \Lambda = \Lambda_0 - \alpha\sqrt{C} - (\Lambda_0 K^{-1})C$$

in which  $\Lambda$  is the equivalent conductance, and  $\Lambda_0$  the equivalent conductance at infinite dilution. These values of  $K$  were substituted into equation (10) and values of  $a_0$  were calculated. These values remained essentially constant with an average of  $6.40 \text{ \AA}$  while the equilibrium constant

varied over fifteen powers of ten. Using this average  $a_0$  value,  $K^{-1}$  values were calculated, agreeing very closely with the conductance values. It was also noted that above a dielectric constant of 43.6 debyes no association takes place.

The theory of ionic association has been extended by Fuoss and Kraus to include formation of triple ions and more complex aggregates.

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1. Harned, H. S., and Owen, B. B., Phys. Chem. of Electrolytic Solutions, (Reinhold Corp., N. Y., 1943) p.42.
2. Fuoss, R. M., Chem. Rev. 17, 27 (1935).
3. Fuoss, R. M., and Kraus, C. A., J. A. C. S., 55, 1019 (1933).
4. Kraus, C. A., Ann. N. Y. Acad. Sc., 51, 789 (1949).

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"Must you always have homework to do?"

## MELTING AND ITS INTERPRETATION.<sup>1</sup>

George P. Flynn, Jr., '57

The process of melting in crystalline solids involves a sharp change from the rigidly ordered crystal structure to the liquid state in which long-range order has broken down, i.e., while in the immediate vicinity of any particular molecule there may be order, the degree of order falls off with distance so that the liquid as a whole is disordered. Any adequate theory of melting must: (1) account for the sharpness of the melting point; (2) describe the structures of the solid and the liquid near the melting point and the relationship between them; and (3) explain the exact nature of the change upon melting.

There are several factors involved in the process of melting. First is a loss of positional order in the crystal, which is the only factor involved in the melting of crystals composed of spherically symmetrical units. Examples of this are the solid forms of the monatomic gases, the metals, and simple ionic salts (such as NaCl). In slightly more complex molecules, melting brings about a decrease in orientational order, i.e., in the alignment of corresponding parts of adjacent molecules. This results when the molecules are not spherically symmetrical. In addition, there are several special melting processes which are discussed separately below.

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<sup>1</sup> Edited from a seminar given February 20, 1956.

For a long time, attempts were made to formulate a rule for melting analogous to Trouton's Rule for the entropy of vaporization. In 1927, Kordes suggested that the entropies of fusion of the elements were periodic within the range of 2 to 3 entropy units. However, this is true only for those elements composed of spherically symmetrical units, as described above. The metals, monatomic gases, and simple ionic crystals have entropies of fusion in this range. The compact polyatomic molecules may be divided into those with entropies of fusion of about 2 or 3 units ( $O_2$ ,  $N_2$ ,  $CO$ ,  $H_2S$ ,  $CH_4$ , etc.) and those with entropies of fusion of about 8 to 10 units ( $CO_2$ ,  $Cl_2$ ,  $SO_2$ ,  $C_2H_6$ , etc.). Both involve orientational changes on melting, but in the first group these occur at transition temperatures below the melting point. Above these transition temperatures there is free rotation in the solid. In this group, therefore, the sum of the entropies of fusion and transition proves to be of the same order of magnitude as the entropies of fusion in the second group.

Rules of this sort are applicable only to substances composed compact molecules. In the homologous series,  $CH_3(CH_2)_nX$ , where  $X$  may be hydrogen or some functional group, it is found that the entropies and heats of fusion are linear functions of the chain length, so that

$$\Delta S_f = \Delta S_0 + n\Delta S_1$$



where  $\Delta S_f$  is the entropy of fusion,  $\Delta S_0$  the entropy of fusion when  $n = 0$ , and  $\Delta S_1$  the entropy contribution due to each additional carbon. Since  $T_f$ , the melting point, is equal to  $\Delta H_f / \Delta S_f$ , where  $\Delta H_f$  is the heat of fusion, it should approach a limiting temperature as  $n$  increases. This temperature has been determined for several such series.

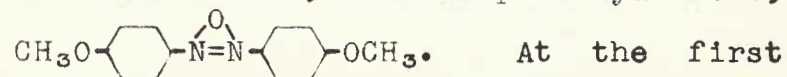
In the case of polymers composed of long, flexible molecules, melting occurs over a wide range. One reason suggested for this behavior is that in the solid only portions of adjacent molecules are believed to be in alignment, so that the molecules melt in segments. Another factor is the phenomenon of premelting, described below.

Measurements indicate that the heat capacities and coefficients of thermal expansion of the solid and liquid states of a substance are almost identical in the immediate vicinity of the melting point. This indicates that the processes of heat intake, and therefore the structures, of the two phases are similar. In addition, X-ray analysis and infra-red scattering suggest the existence of short-range order in the liquid just above the melting point. It seems, therefore, that the solid and liquid in this range have similar structures, so that the liquid is spoken of as quasi-crystalline.

In some substances (e.g., Zn, Cd, paraffin and cyclic hydrocarbons), a phenomenon known as premelting appears to take place. Curves of the heat capacity and coefficient of expansion show

sharp increase just below the melting point. Similar anomalies are also observed in the density and diamagnetic susceptibility. The theory that these are due to impurities which are more soluble in one phase does not fit the observed data and cannot be applied to all cases. It is probably caused in the solid by flaws in the crystal lattice (a partial breakdown of order), and conversely, by residual order in the liquid. Premelting becomes important when the entropy of fusion is large, and thus is of dominant importance in polymers.

Among the special cases of melting are the so-called liquid crystals, or mesomorphic states, of substances which appear to melt in two or more steps. The intermediate stages show some of the properties of the liquid and the solid, often polarizing light or flowing in distinct planar layers. These substances are composed of long, rod-like molecules, usually containing several aromatic nuclei, such as p-azoxyanisole,



transition point, these molecules lose their periodic arrangement but not their orientation. This is lost in the final change to the liquid. While unusual, these phenomena present no difficulty in interpretation. Other unusual types of transition include the solidification of liquids into glasses, the vitreous forms containing strong intermolecular linkages which cannot be readily formed again once broken, and some rubberlike polymers which crystallize on stretching.

Current theories of melting are applicable only to the simplest cases i.e., of spherically symmetrical molecules. The best theory, that of Lennard-Jones and Devonshire, assumes a simple cubic lattice of so-called  $\alpha$ -sites, with an imaginary interpenetrating lattice of  $\beta$ -sites. In the solid all the molecules are on  $\alpha$ -sites, while melting occurs when there exists a completely random distribution over both the  $\alpha$ -sites and the  $\beta$ -sites. The related theory of Roseveare, Powell, and Eyring considers the liquid as a mixture of molecules and holes, distributed at random over the crystal lattice. This theory assumes that the increase in volume upon melting is caused solely by the formation of these holes.

Several explanations of the sharpness of the melting point have been advanced. The simplest and most obvious is the geometrical effect of the displacement of a few molecules, upsetting the entire lattice. However, this can serve only as a partial explanation. More important is the interaction between molecules, which makes it easier for several nearby molecules to change their sites simultaneously rather than separately. Finally, according to Lennard-Jones and Devonshire, the pressure-volume isotherm at the melting point follows an S-shaped curve, similar to van der Waals isotherms. On such a curve, the area in the S-shaped region represents an unstable system which breaks up into two phases.

The equations of Lennard-Jones and Devonshire can be used to calculate

quite accurately the melting parameters of simple substances, such as argon, given knowledge of one property. However, this theory is essentially an oversimplification. In particular, the theory fails at high pressures since it predicts a critical point, no evidence of which has yet been found. Nevertheless, this theory is the best thus far advanced to explain the phenomenon of melting.

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Gather ye products while ye may

For time brings only sorrow;

Thy stuff will crystallize today -

Polymerize tomorrow.

-The Amalgamator



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