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Order from Chaos

The theory of regular solutions is a "result of giving to ordinary human effort a direction and purpose."

Joel H. Hildebrand

There are scholars who, looking at the scientific enterprise from the outside, see the huge and ever growing body of factual knowledge only as a collection of fragments, and they cry for integration and synthesis. If they would come inside, if only for a sojourn, they might see that we insiders are busily engaged in the very activity that they exhort us to undertake; we are building fragments of information into structures of great beauty, comparable as achievements of the human mind and spirit with the greatest works of art and literature. These structures are a major part of humanism. To define science as technology, or as "classified information," as in a certain dictionary, is as misleading as it would be to characterize the Parthenon as calcium carbonate.

I propose mainly to describe part of what I have been doing during some 70 years. Like many scientists, I began at an early age. I am still at it at 83, thanks to able young collaborators, to the United States Government which has supported the work, and to my university, which winks at my theoretical senility and generously provides office and laboratory.

The Colors of Iodine Solutions

Most of the order that has been brought into contemporary chemistry during these years has been constructed out of what was chaos when I was a student. The book that I studied in high school contained no Periodic System. In my freshman course in the university, the atoms were still immutable. Ostwald in Germany was maintaining that since atoms could not be seen it was not proper even to talk about them. After I returned in 1907 from a postdoctoral year in Berlin to teach the first course in physical chemistry offered at the University of Pennsylvania, I was barely suffered to mention ions. The head of the department—in those days they were "heads," not chairmen—said, "The real question is, can you analyze sulfuric acid; I don't care whether you do it by ionic theory or by mass action, but can you analyze it?" The chemistry curriculum was designed chiefly to train analytical chemists. I had matriculated, fortunately, in the College of Arts and Sciences, with a joint major in chemistry and physics. I thus escaped an excessive dose of a kind of chemistry that from my present standpoint was either unimportant or untrue. The physics, mathematics, history, and literature that I took in its stead made me a better person and, ultimately, even a better chemist.

Instead of devoting myself to learning the recipes that made up the content of courses in the analytical chemistry of those times, I turned to things that I wanted not just to know but to understand. It is this that differentiates a scientist from a practitioner. There is nothing invidious about this difference; I have the greatest respect for my physician; his vast knowledge of physiology, anatomy, and medicine is more than I could ever have hoped to acquire. I have not had to answer other persons' questions; such standing as I have among scientists has been based upon questions and answers that I have devised.

My attention was early attracted by the beautiful colors of iodine, in the vapor and in its solutions. In many solvents it is violet, as it is in the vapor; in benzene it is red; in alcohol, ether, toluene, and xylene it gives various shades of brown; in water it is pale yellow. Several explanations had been proposed but not supported by experimental evidence.

I performed a simple experiment to determine whether the brown colors resulted from the union of molecules of iodine with those of the solvent to form a complex. Iodine dissolves in bromoform, giving a violet solution which turns brown upon addition of small amounts of alcohol. Substances dissolved in bromoform depress its freezing point by amounts depending upon their concentrations. I determined the extent of this depression with known concentrations of iodine and alcohol, first separately, then together. I found (*1*) that the depression when both were present was much less than the sum of their separate depressions. It was clear that some of the molecules had united to form molecules of complex, thus reducing the total number of molecules in the mixture.

The next question was: What is the formula of the complex? I made a dilute solution of iodine of known concentration in carbon tetrachloride, in which it is violet, indicating absence of any complex. Upon addition of successive small amounts of alcohol, the color changes by steps to brown. I could measure the concentration of brown complex in a colorimeter by

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The author is emeritus professor of chemistry at the University of California at Berkeley. This article was originally delivered as an address at Dickinson College, 19 March 1965, when the author received the Joseph Priestley award.

using blue light. I found that the concentrations of free iodine, of complex, and of free alcohol were related by an equilibrium constant for a complex containing one molecule each of iodine and alcohol, as seen in Table 1. The one-to-one composition was found for complexes with other solvents. This investigation, published in 1909, was my first plunge into theory of solution of nonelectrolytes, an enterprise which, in its manifold aspects, has ever since engaged much of my attention. I wish to relate some of the main events of my scientific biography, with emphasis upon my tactics and strategy; it is not my purpose here to teach physical chemistry.

With reference to tactics, I offer, first, this comment. I undertook these experiments in order to get answers to significant questions, not just to measure something. I have refereed many applications for research grants. Some propose to gather data with no apparent further purpose. They show little evidence of scientific curiosity; one suspects that some of them may have been initiated by an administrator's saying to a member of the faculty: "Look here, Bill, we ought to get in on some of this government money; can't you think up a project?"

I do not deprecate the gathering of scientific data. I only urge that they be gathered with a purpose; one should think up good questions to investigate. Reliable measurements are the building materials for scientific structures, but theory and experiment should pull together like a team of horses. Data gathered more or less at random are not those most likely to be useful in extending the conceptual structure of science. One might suppose that among the vast accumulations of data on solubility that are available I could have found most of what I have needed in order to test my hypotheses, but that has not been the case. Most of the figures I have wanted I and my co-workers have had to determine ourselves.

Texts on quantitative analysis have not always furnished the necessary methods. When, for example, I wished to determine the solubility of perfluoroheptane in bromine, and of water in liquid phosphorus, I had to invent suitable procedures.

Vapor Pressures of Amalgams

At about the time that I started to investigate solutions of iodine, I began also a study of the vapor pressures of mercury over its liquid amalgams. I thus plunged more deeply into the problems presented by the properties of liquid mixtures. Very little was then known about these properties. Van Laar (*2*), in Holland, had made a significant beginning in 1906, but his good thermodynamics was mixed inextricably with the inadequacies of the van der Waals equation. Nernst was basing his treatment of solutions upon the concept of osmotic pressure, according to which the solvent merely affords space in which the solute can exert an osmotic pressure equal to the pressure it would exert as an ideal gas in the same volume. Nernst even used this osmotic pressure law to supply a theoretical basis for Raoult's empirical law for vapor pressure. Dolezalek (*3*) "explained" the departures of the partial vapor pressures of nitrogen and argon from their liquid mixtures as the result of an equilibrium between single and double molecules of argon! Rothmund (*4*) published a book on solubility in 1907 in which he wrote: "Very little can yet be said about the relation between solubility and chemical nature."

Table 1. Equilibrium between the concentration (C) of alcohol, iodine, and 1 : 1 complex in carbon tetrachloride. K, equilibrium constant.

Alcohol (C_1)	Iodine (C_2)	Complex (C_3)	$K = \frac{C_3}{C_1C_2}$
595	1.53	1.14	1.25
194	2.21	0.52	1.21
130	2.36	.39	1.27

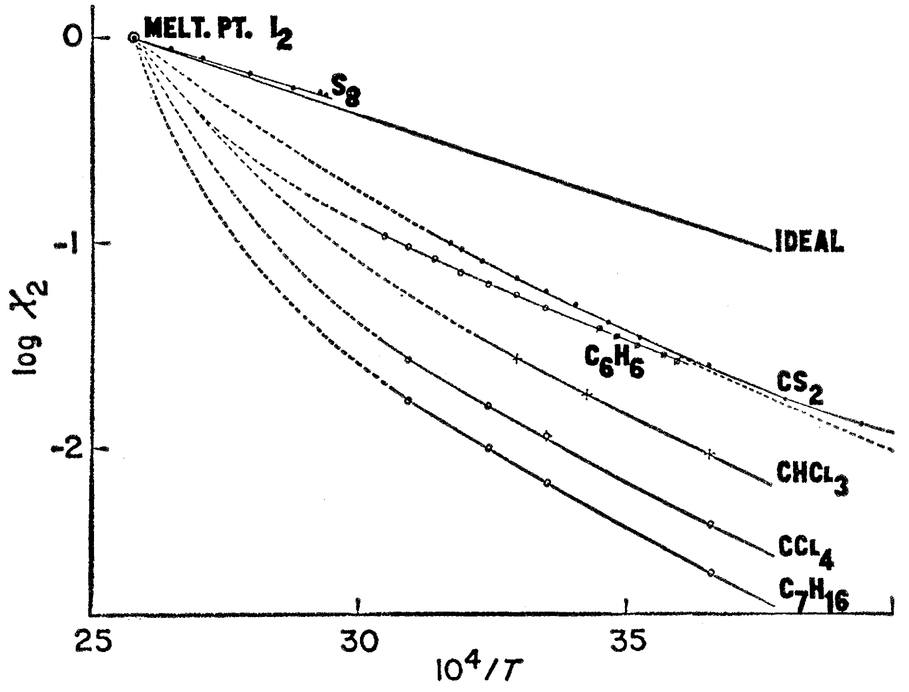


Fig. 1. Solubility of iodine, 1920. [Reprinted from *J. Am. Chem. Soc.* (*7*), by permission of the copyright owners, the American Chemical Society]

Most physical chemists in those days were busy investigating solutions of electrolytes in water; therefore, I had a pretty clear field, with few competitors. There are advantages in pioneering into unexplored territory instead of joining a stampede into a newly opened field.

My first result (*5*) from a study of amalgams showed that the vapor pressures of mercury from zinc amalgams at 300°C plotted against the mole fraction of zinc were larger than they would be if they followed Raoult's law. I derived an equation for a line running through the observed points by assuming that there are single and double molecules of zinc in equilibrium, a guess that seemed more probable in the case of zinc than in that of argon.

Now any investigator who succeeds in deriving a theoretical equation that fits his experimental results is likely to pat himself on the back and feel tempted to infer that he has proved his theory to be true. I confess I did.

But hear what happened to my theory soon thereafter. In 1916 I published a paper entitled "Solubility" (*6*).

By then I had discovered a number of solutions that depart more or less widely from Raoult's law, although any changes in molecular species are out of the question. My choice of iodine as a common solute was in this respect very fortunate, since color provides an unmistakable criterion. Its solubilities in violet solutions at 25°C range all the way from 5.58 mole percent in carbon disulfide to 0.018 mole percent in perfluoroheptane, although its absorption spectrum in both is virtually identical with that of iodine vapor.

Such considerations led me to abandon my theory of zinc amalgams published only 4 years earlier, and I wrote (*6*):

> If we seek a clue of a kinetic nature to deviations from Raoult's law, we find it in the limitation stated earlier while giving the kinetic justification for the law, namely, that the molecules must be sufficiently alike so that they are under the same forces in the mixture as in the pure liquids. It has seemed to the writer that the most satisfactory concept to serve as a base for [likeness] would be found in internal pressure.

Applying this concept to my zinc amalgams, and, by then, to others as well, I later derived an equation quite different from the former one. But by adjusting a single parameter in each equation, the equations could be made to fit the experimental points equally well. This was a tie between two utterly incompatible theories. This experience taught me a very important lesson: agreement of experiment with theory does not "prove" that the theory is "true"; it merely furnishes some evidence that the theory may be adequate for dealing with another case of the same kind. The probability that a theory is adequate grows with the number of successful cases of agreement. A law of science is not a piece of legislation that phenomena are bound to obey. There is no penalty for being "abnormal."

There are cigarette smokers who comfort themselves by adopting the statement of the manufacturers that "it has not been proved that cigarette smoking causes cancer." Of course not; causes and effects cannot be connected with absolute certainty; all honest scientific predictions are subject to probability. The odds are extremely high for predicting an eclipse, good for death rates, poor for stock prices, near zero for the time when John Doe will die.

Regular Solutions

But getting back to solutions, the steps in the making of order out of near chaos offer significant examples of the logic of experimentation. New order was revealed to me by trying new methods of plotting. The common method of earlier years was simply to plot concentration against temperature. In 1920, Jenks and I (*7*) plotted solubilities of iodine in a series of solvents as logarithm of mole fraction against the reciprocal of the absolute temperature. Our plot for iodine is shown in Fig. 1. We pointed out that (i) the lines for all but the benzene solutions form a family of curves; (ii) their divergence from the line calculated for an ideal solution is in order of increasing difference of internal pressure; (iii) the line for benzene solutions, which are red in color, does not belong to the family, because complexing raises the solubility of iodine in benzene above its solubility in chloroform, which is the solubility it would be expected to have if there were no complexing.

Further determinations added more curves to the family, and the curves for the solubility of sulfur, stannic iodide, and other substances were found to be grouped in similar families. The concept of internal pressure was serving to bring some order into the mass of data on solubility. The next forward step required the invention of concepts that could serve as bases for deriving a general equation for the lines in these families. The regularity evident in these curves suggested that the solutions be designated "regular solutions." Several of my British friends have adopted my term but not my definition, each defining it in a different way. I have gently scolded them for it.

Well, what is regular about regular solutions? In proposing the term in 1929 I wrote (*8*), in part:

> From our picture of a regular solution as one in which orienting and chemical effects are absent, and in which the distributions and orientations are random, just as in the ideal solution, we may conclude that the probability [of the molecules of each component] is the same in the two solutions, and, therefore, that the difference in entropy is zero. We cannot expect this conclusion to hold unless the random distribution of molecules persists. We may expect, further, that a small correction should be applied to take care of the change in entropy accompanying changes in volume . . . or, we may state

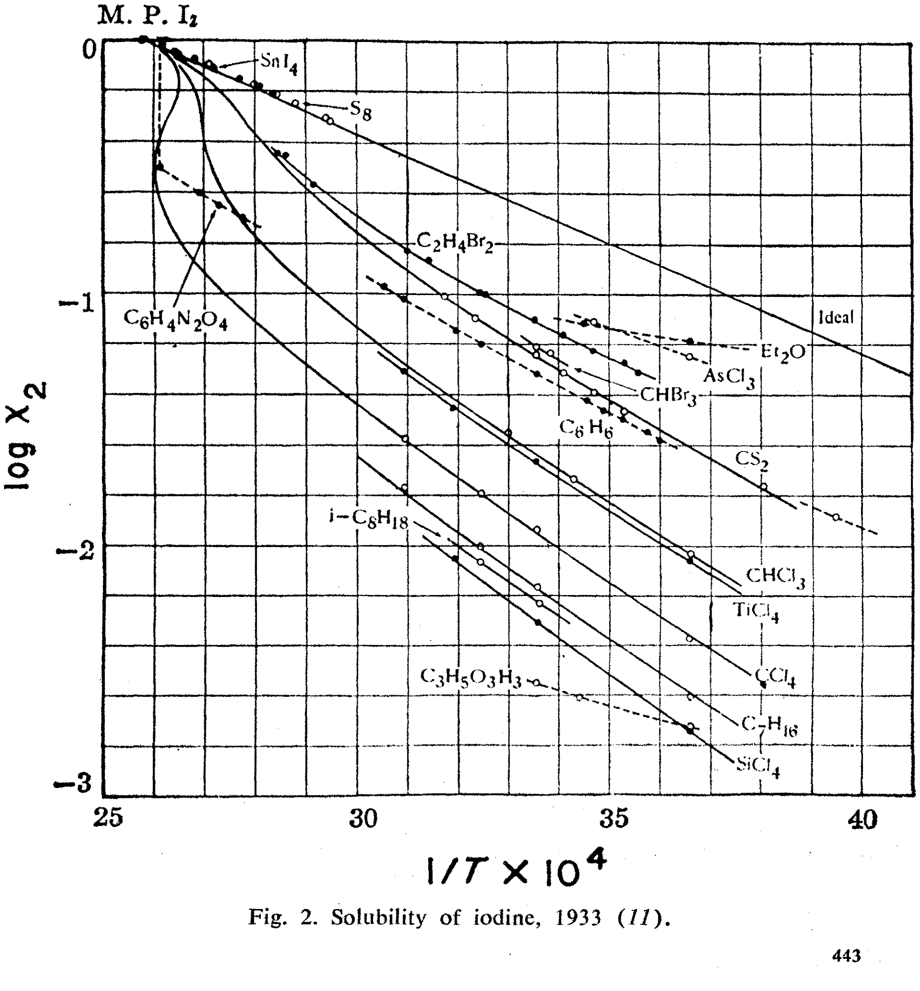


Fig. 2. Solubility of iodine, 1933 (*11*).

our principle in the following form: A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution, the total volume remaining unchanged.

As I mentioned before, Van Laar (*2*) had made a significant beginning in 1906, but he based everything upon the van der Waals equation and used differences in critical pressure as his main criterion of deviation from Raoult's law. Had he performed experiments he might have discovered that chlorine and carbon tetrachloride obey Raoult's law although their critical pressures are 76 and 45 atmospheres, respectively, whereas carbon tetrachloride and methanol, with nearly identical critical pressures, are so unlike as to yield two liquid phases.

Scatchard (*9*), in 1931, combined regular solution entropy with a formulation of the heat of mixing based upon the Berthelot (*10*) relation of 1898, which expresses the interaction energy between unlike molecules as the geometric mean of the interaction energies of the like molecules. This equation had the form of the Van Laar equation but with different meanings assigned to the parameters. In 1933, Scott Wood and I (*11*) derived the same equation for energy of mixing on the basis of the so-called "distribution functions," which relate the energies of vaporization of pure liquids and of their mixtures to the attractions between pairs of like and pairs of unlike molecules. The resulting equation has been called the "Van Laar-Scatchard-Hildebrand equation."

Solubilities in other liquids were added from time to time, till, by 1933, the plot (*12*) became as shown in Fig. 2. Note that the equation for iodine in carbon tetrachloride gave an S-shaped line near the melting point of iodine. This promised that at higher temperatures two liquid phases could coexist. Indeed, the equation permitted calculation of their critical mixing temperature and composition. I found this impossible to verify by visual observation; the solutions were completely opaque, even in capillary tubes. I had recourse, therefore, to an indirect method. I sealed in glass tubes

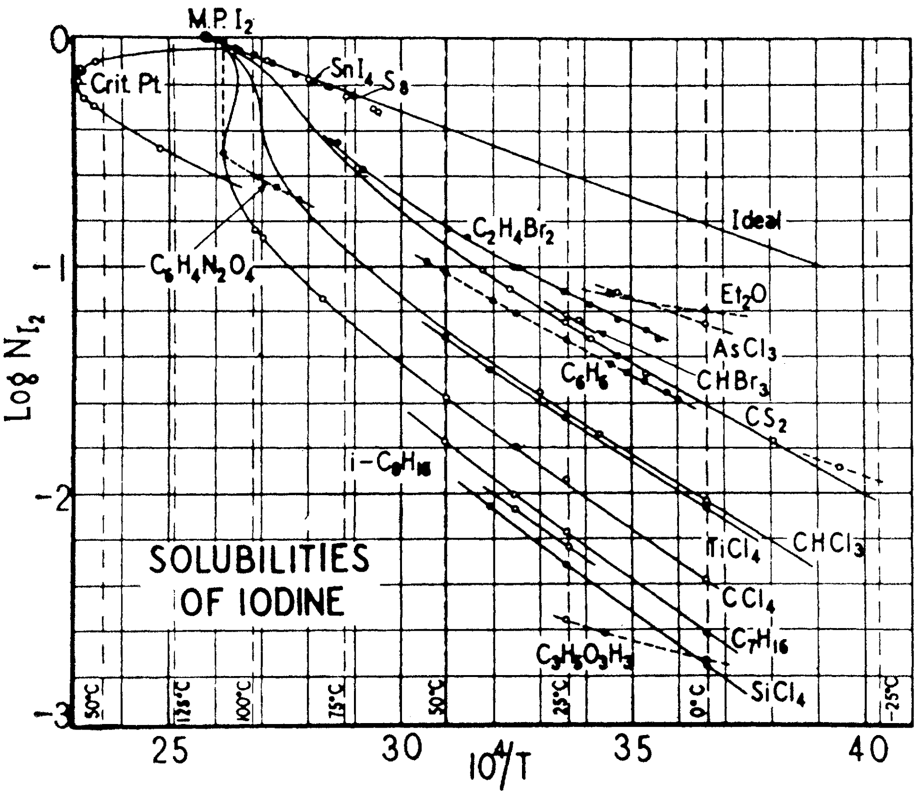


Fig. 3 (top left). Solubility of iodine, 1937 (*14*).

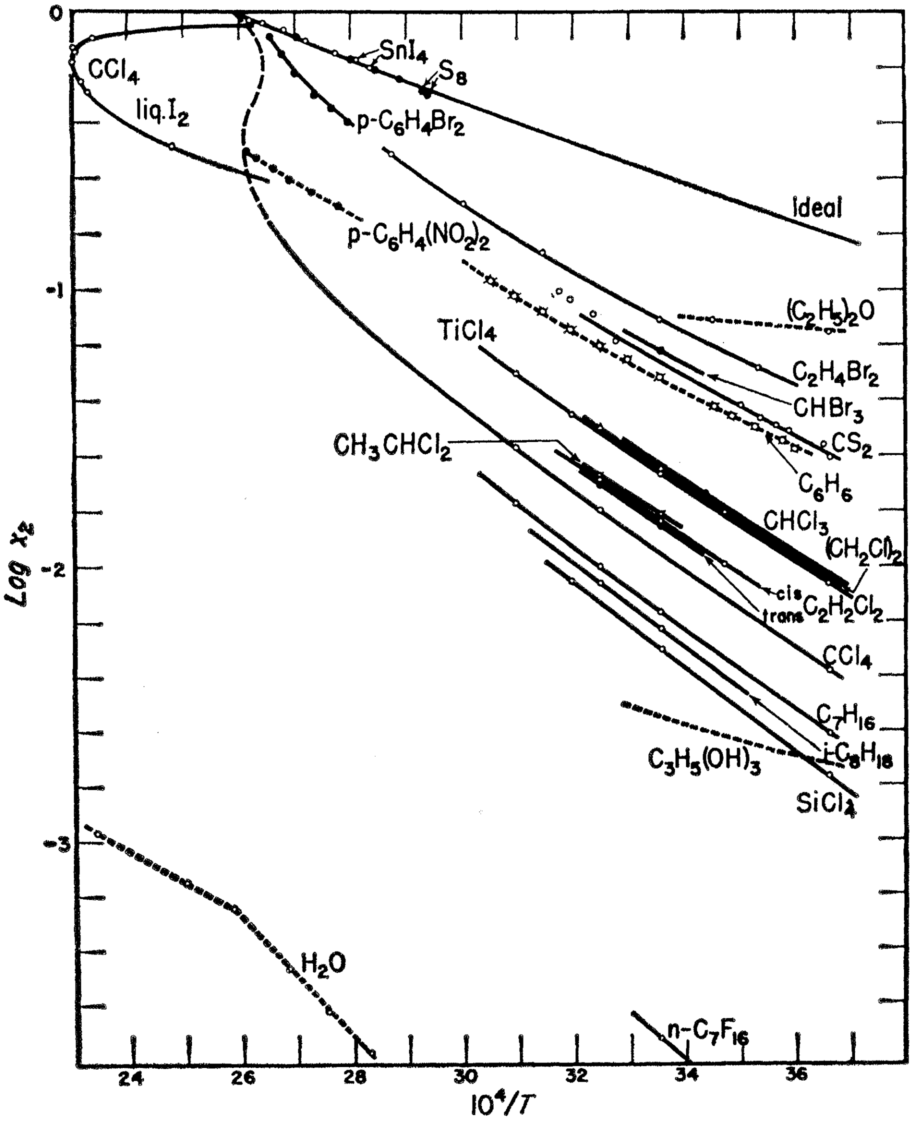


Fig. 4 (bottom left). Solubility of iodine, 1948. [Reprinted from *J. Am. Chem. Soc.* (*16*) by permission of the copyright owners, the American Chemical Society] mixtures of iodine and carbon tetrachloride of different compositions. I made a sort of cradle that held a tube in an inclined position, balanced against a weak spring. A tiny mirror attached to the cradle reflected a beam of light onto a scale. The cradle with its tube was heated in an air bath to a temperature well above the predicted two-liquid region; it was then rocked to make the composition of the mixture uniform throughout. The temperature was then allowed to fall very slowly while I took readings of the position of the light spot on the scale. A plot of scale readings against temperatures showed a break which signaled the separation of an iodine-rich liquid that flowed to the bottom of the tube, creating a torque. By determining this temperature for the series of tubes containing mixtures of known composition, it was easy to construct the liquid-liquid solubility curve (*13*). This was done in 1937. The comprehensive plot published in 1939 (*14*) (Fig. 3) includes this loop.

When we got under way again after World War II, H. A. Benesi and I (*15*) sought answers to two important questions. One concerned the solvent powers of the fluorocarbons that had become available. My former collaborator, George C. Cady, had told me that heptane and fluoroheptane are so different as to form two-liquid mixtures, a phenomenon I had found rather rare among nonpolar liquids. I wondered whether our solubility equations would be overstrained by fluorocarbons. Now the thing to do in such a case is to put your theory under maximum strain—don't leave that to your competitor—so we selected iodine as our test solute. The colors of saturated solutions of iodine in these two heptanes indicate its extremely small solubility in the fluorocarbon. Nevertheless, it is pure violet and obviously regular. Benesi's point is seen in Fig. 4, the version of 1948 (*16*). The point is far from the lines for the other solvents, but we were delighted to find it close to where the equation predicted it would be. Since then the point has been stretched to a line and other solvents have been found to occupy the gap.

The other question that Benesi and I raised was this: If a solvent molecule contains two polar groups, does their effect upon solvent power depend upon the individual groups or upon the overall dipole moment of the whole

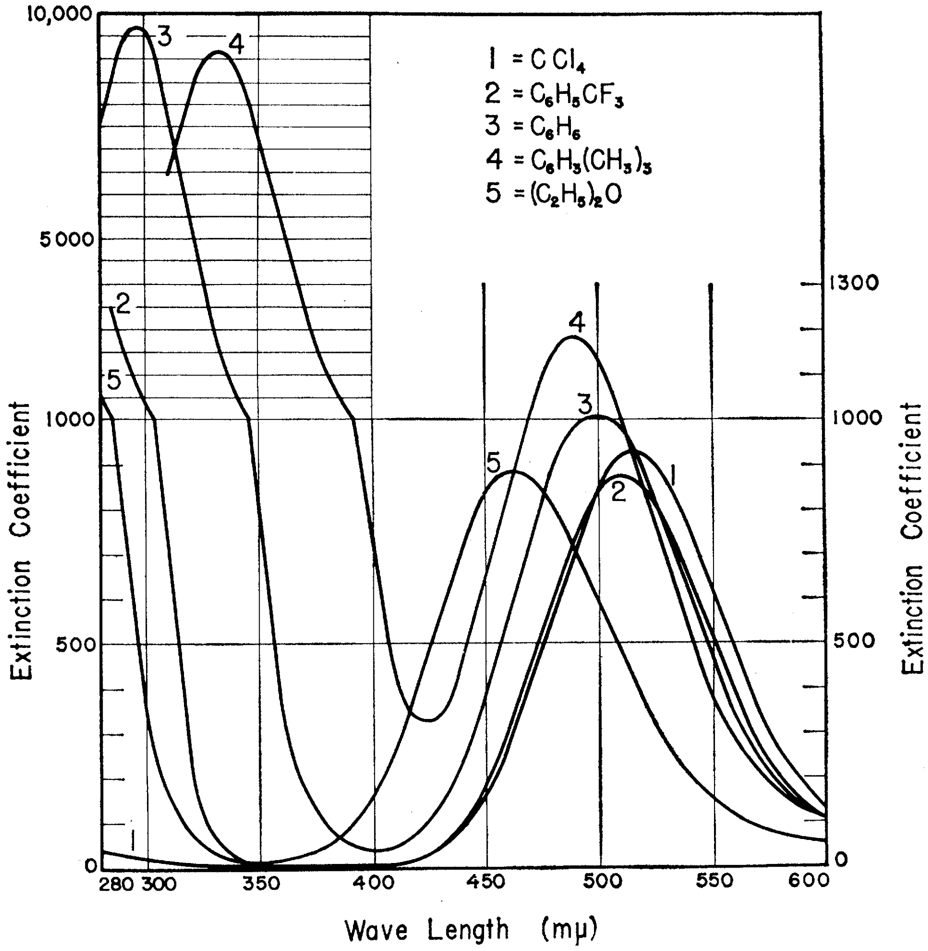


Fig. 5. Ultraviolet absorption by complexes. [Reprinted from *J. Am. Chem. Soc.* (*16*) by permission of the copyright owners, the American Chemical Society]

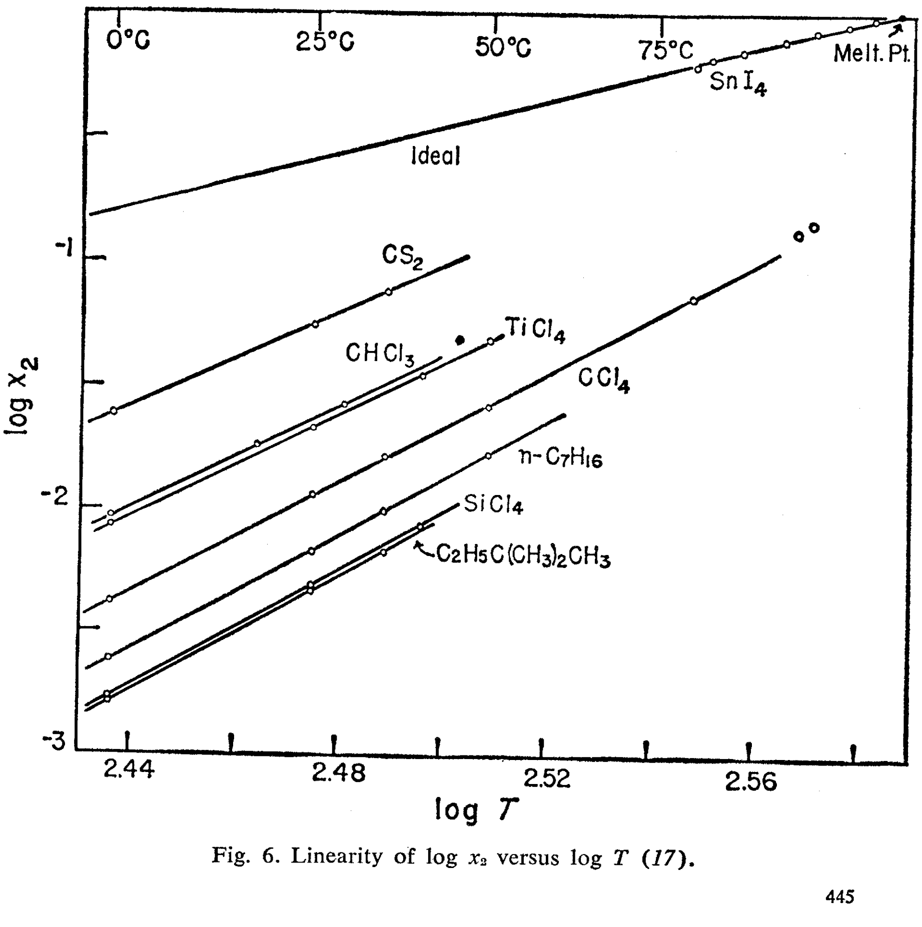


Fig. 6. Linearity of log x_2 versus log T (*17*).

molecule? To answer this question we determined the solubility of iodine in *cis-* and *trans-*dichloroethylenes. In the former the two polar carbon-chlorine bonds lie in the same direction, and reinforce one another; in the *trans-* isomer they lie in opposite directions, making the overall moment zero. Thus the solubility of iodine must be affected by the two polar groups individually, since it is virtually the same in both liquids.

Ultraviolet Absorbtion by Complexes

The next major forward step came as an unexpected answer to the question, Why is the solution in benzene red? All the other liquids that I then knew about which gave nonviolet solutions are very polar. They include alcohols, acids, ethers, and ketones. Benzene, however, has zero dipole moment. It occurred to me that this might be a case of Lewis acid-base interaction, in which an electron-acceptor takes electrons from a donor. The fact that an iodine atom can accept more than an octet of electrons is illustrated by periodates. But could benzene be a donor? I did not know, but the staff of my department represents a powerful collection of chemical lore, and all I had to do was ask Melvin Calvin; he said that benzene could be a donor, and when I asked whether substituted methyl groups increase donor strength, he answered yes to that also. Benesi then prepared solutions of iodine of the same concentration in carbon tetrachloride, benzene, toluene, *m*-xylene, and mesitylene, the last in two tubes, one of which we heated.

We next undertook to find out what an absorption spectrometer could show in these colors which our eyes could not see. Figure 5 shows what the spectrometer revealed (*16*). This has become a historic plot; it opened the way to scores of investigations by other scientists. Our eyes had seen only the visible region, in the right-hand half of the plot, but the spectrometer revealed the hitherto unknown strong bands in the left. This was a complete surprise. The visible peaks are merely shifted by the solvents; the ultraviolet peaks are those of new molecules, complexes between iodine and solvent. This study, first published in detail in 1949, opened up a new and powerful means for studying such complexes and has revealed the existence of complexes in mixtures where they had never been suspected.

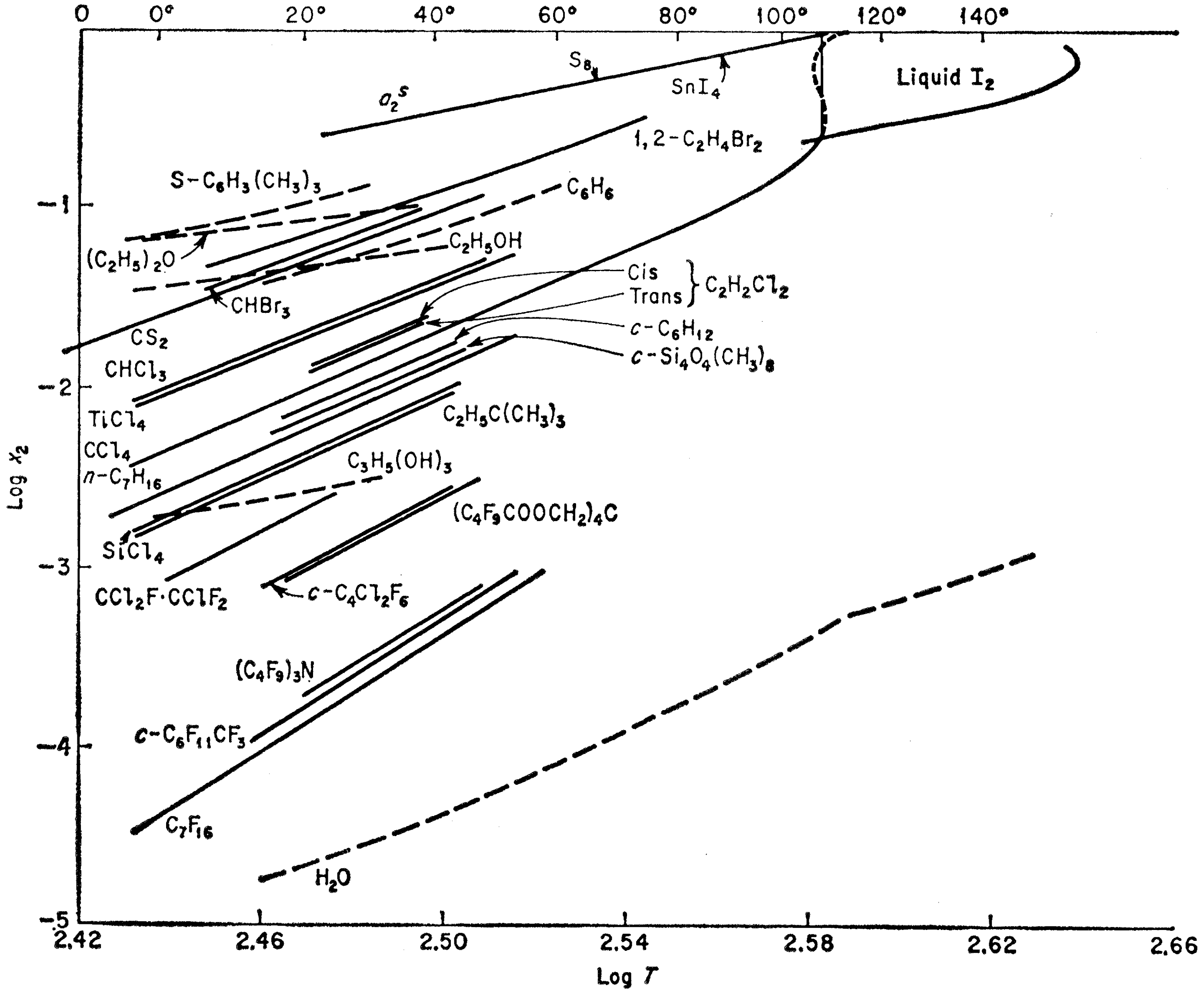


Fig. 7. Solubility of iodine, 1962. [Reprinted from J. H. Hildebrand and R. L. Scott, *Regular Solutions* (© 1962), by permission of Prentice-Hall, Inc., Englewood Cliffs, New Jersey]

Departures from Regular Solution Behavior

In 1951 I invented *(17)* still another new way for plotting solubilities (Fig. 6). The horizontal scale is now the logarithm of the absolute temperature. The lines are now straight, except near the melting point of iodine; this is a great advantage, since the slope of a straight line can be determined more precisely than the slope of a curved line; this slope is very significant since, multiplied by the gas law constant, *R*, it gives the entropy of solution, the function that characterizes regular solutions. Figure 7 shows all the data we had in 1962 plotted in this way *(18)*.

Entropy is the thermodynamic function most closely related to structure, and maximum entropy of mixing indicates that the molecules of the mixture are in a state of maximum disorder. The next step, accordingly, was to plot *R* times the slopes of the lines in Fig. 7 against the logarithms of the mole fractions of iodine at 25°C. The resulting plot is seen in Fig. 8; it was published in 1956 by Glew and myself *(19)*.

Table 2. Partial molal volume of I_2, v_2, in liquids of widely varying molal volumes, v_1; 25°C.

Liquid	$\bar{v}_2$	v_1
$CHCl_3$	66	81
CCl_4	67	97
$SiCl_4$	67	115
i-C_8H_{18}	67	166
c-$Si_4O_4(CH_3)_8$	67	312

This manner of plotting affords a sensitive test of complexing; the points for the solutions in the dichloroethanes and ethylenes, which, in the former plot, had appeared to belong among the regular solutions, are here seen to indicate weak complexing. A reexamination of the colors of these solutions revealed that they are not quite violet. The points for the solutions in benzene, toluene, *p*-xylene, and mesitylene deviate increasingly in order of basic strength.

I applied this method of plotting *(20)* also in order to learn whether the entropy of mixing depends upon the relative size of the molecules. One sees in Fig. 9 that the entropy of solution of iodine gives points all falling on the same line although the seven solvents have molal volumes ranging from 104 to 540 cubic centimeters. This independence is seen also in Table 2, which shows that there are no larger "holes" in liquids of large molecules ready to receive the small molecules of iodine; the iodine molecules must dig their own space. In the theory of regular solutions, there are no "holes."

Two years ago Hiraoka and I *(21)* published still another way of scrutinizing the solubilities of iodine at 25°C. We plotted $-\log x_2$ as ordinate against $(\delta_2 - \delta_1)^2$ abscissa, the variables in the simple equation for *regular solutions*:

$$RT \ln a_2^s/x_2 = v_2\phi_1{}^2(\delta_2 - \delta_1)^2. \qquad (1)$$

Here x_2 is the mole fraction of iodine, a_2^s is the activity of solid iodine referred to supercooled liquid as the standard state, 0.256; v_2 is its extrapolated molal liquid volume, 58.5 cubic

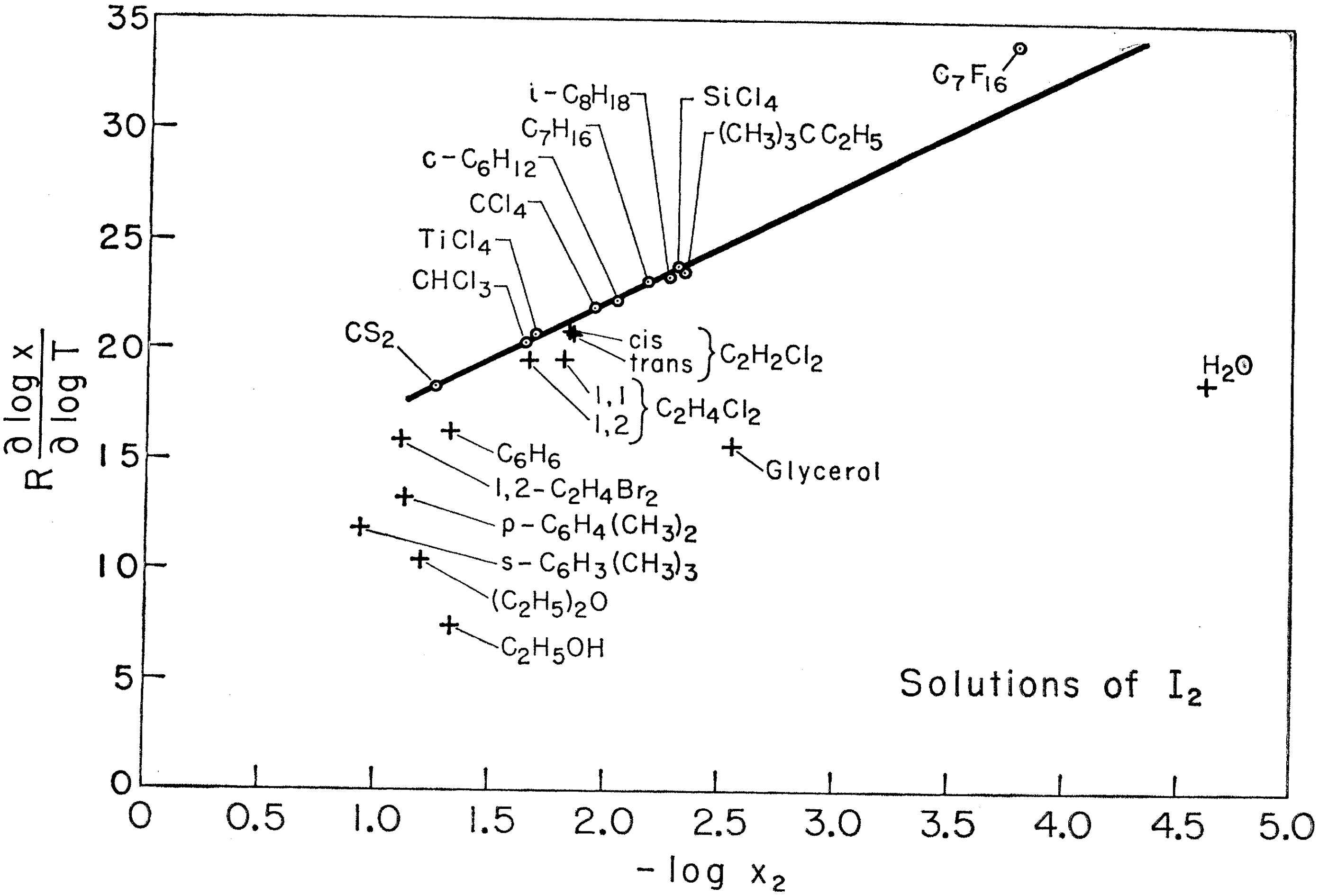
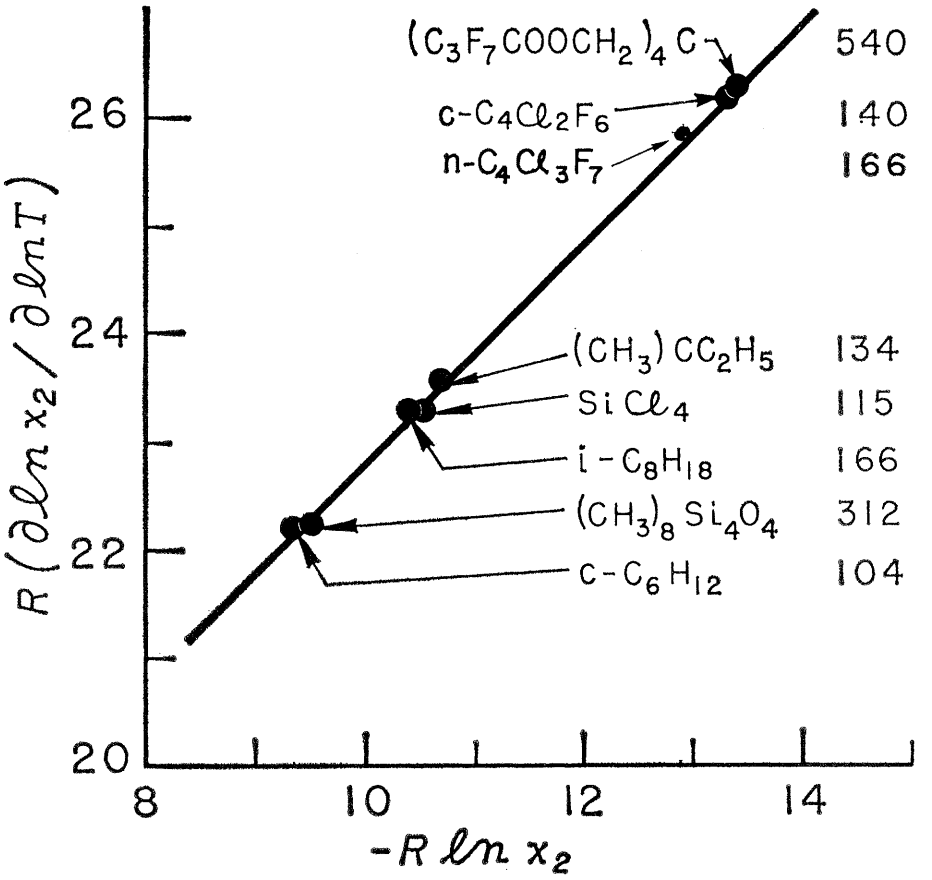
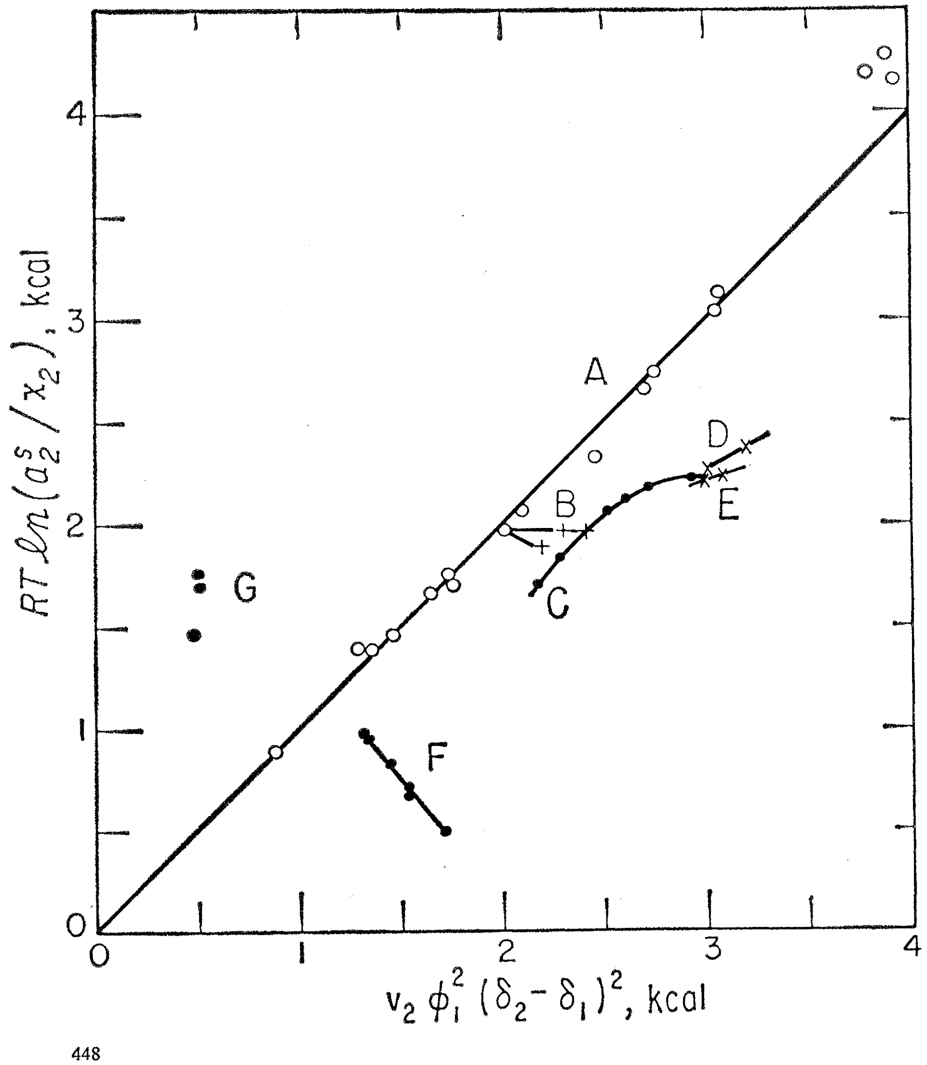


Fig. 8. Irregular entropy of complexes. [Reprinted from *J. Phys. Chem.* *(19)* by permission of the copyright owners, the American Chemical Society]





centimeters; ϕ is the volume fraction of solvent; the δ's are *solubility parameters*, calculated from energy of vaporization per cubic centimeter, and $\delta_2 = \Delta E^v/v$. For iodine, $\delta_2 = 14.1$. This form of plotting was used again in a paper with K. Shinoda and shown when I delivered the Priestley award lecture.

After delivering the lecture I decided that it would be still more revealing to plot against each other the functions on the two sides of Eq. 1, which have the dimensions of calories per mole. The result is seen in Fig. 10. We see that there are six groups of solutions. The points for 14 violet solutions fall on line *A*. These solutions conform closely to the two major assumptions embodied in Eq. 1: (i) ideal entropy, and (ii) interaction potential between iodine and solvent conforming to the geometric mean

$$[(\Delta E_1^{vap}/v_1)\ \ (\Delta E_2^{vap}/v_2)]^{\frac{1}{2}}.$$

This potential is a little weaker in the case of the three fluorocarbon solvents at the top of line *A*. Groups *B, C, D,* and *E* are violet solutions in aliphatic hydrocarbon solvents that diverge from the line by amounts depending on ratios of methyl to methylene hydrogen. Group *F* consists of nonviolet solutions in aromatic solvents, benzene to mesitylene. Group *G* consists of solutions in three solvents with dielectric constants 9 to 10 that increase their ΔE^{vap} without improving their solvent power for iodine.

This plot reveals an amazing amount of order, not only the order seen on line *A*, but also the order involved in the different source of divergence from line *A* of each of the other groups. It illustrates beautifully what Gilbert Lewis called "the result of giving to ordinary human effort a direction and a purpose" (*22*).

I trust that the impression I have given is one of the building of a coherent structure. Parallel with those investigations we have carried on similarly systematic studies of solutions of other solids, of gases, and of liquids. All of our findings have been consistent with the concept that in pure, nonpolar liquids and their noncomplexing mixtures, the molecules are in a state of maximum disorder. We have

Fig. 9 (top left). Entropy independent of molal volumes (*20*).

Fig. 10 (bottom left). Systematic departures from complete regularity.

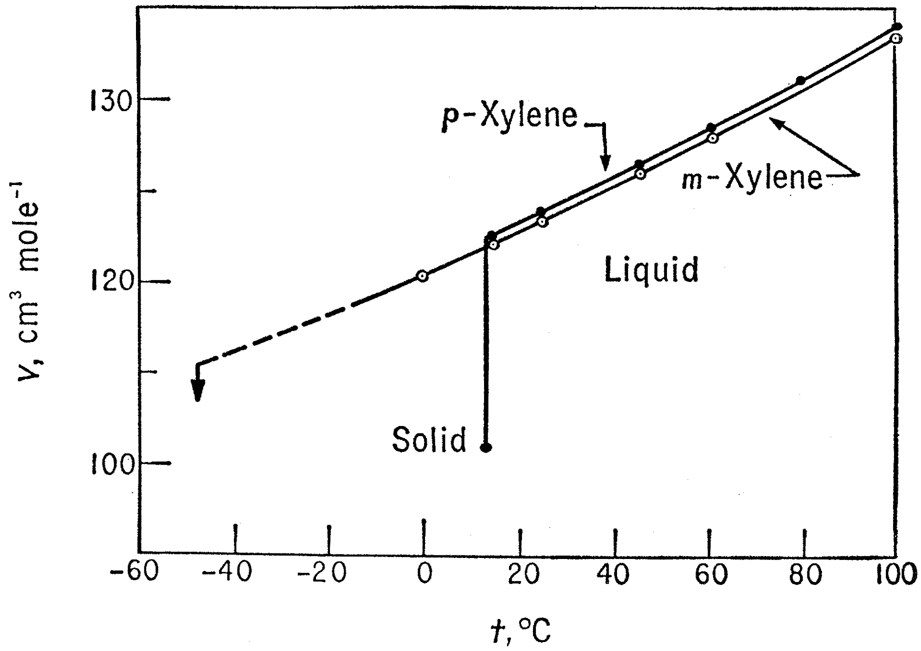


Fig. 11. Molal volumes of xylene isomers (*23*).

tested this concept in a variety of ways. One strong piece of evidence is to be seen in the fact that although the melting point of phosphorus is 44.1°C, we have observed drops of it still liquid at −70°C. If the liquid contained any trace of solid-like structure, as has been claimed by some theoreticians, it is scarcely conceivable that these structures would not grow into full-fledged crystals when cooled 100° below the freezing point.

Metaxylene and paraxylene have furnished another clear test, published by Archer and myself (*23*). Their molecules differ only in the position of their two methyl groups. In their common liquid range, they differ but slightly in boiling point, density, viscosity, and heat capacity. Their molal volumes are shown in Fig. 11. The molal volumes differ by only 0.5 cubic centimeter all the way from the boiling points of the two xylenes to the freezing point of paraxylene, 13.2°C. But paraxylene, because of the shape of its molecules, can pack into crystals more tightly, freezing with a contraction of 16.7 percent, while metaxylene must be cooled to −47.9°C before it can freeze. Now if there were any microcrystals present in either liquid at, say, 14°C, they would surely have to be far more numerous in the para- variety, and its line would have begun its downward plunge. Instead, there is no indication even at 14°C of what can happen to it at 13.2°C. Smith and I (*24*) found that the viscosities of these isomers are closely parallel clear down to 18°C.

I shall mention only one of several further pieces of evidence that in simple liquids there are no "cells," "lattices," microcrystals, "holes," "vacancies, or "solid-like molecules."

In 1953 we turned to diffusion for further evidence. According to the lattice model, molecules move from one lattice site to another in jumps of about one diameter in length, like a man changing seats in a nearly full auditorium; he can move only if a seat next to him is vacant or if he is able to eject his neighbor, which, of course, requires a certain amount of energy. According to our picture the molecules are jostling one another in purely random fashion, like persons in a crowd, moving between collisions in short, irregular directions, taking what we call "random walks." They do just what we can actually see in the Brownian motion of a colloidal suspension.

We determined the diffusivity of iodine in carbon tetrachloride over ranges of pressure and temperature which permitted us to calculate the effect of temperature when volume is kept constant, and there is no change in the number of any "holes" present. We later determined the self-diffusion of carbon tetrachloride under the same conditions. We found in both cases that the motive energy is the mean kinetic energy of the molecules and that there is no relation between the lengths of calculated jumps and molecular diameters.

I said in a recent address to the American Philosophical Society (*25*):

> The moral to be drawn from this conflict is that a model should be regarded as suspect if it yields inferences in serious disagreement with any of the pertinent

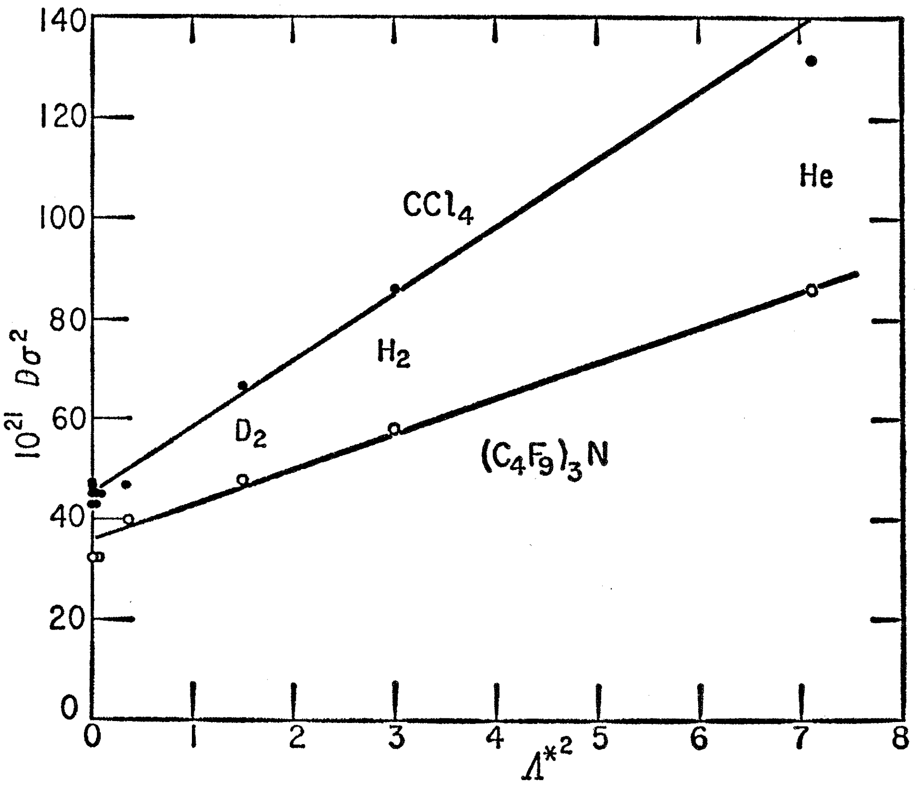


Fig. 12. Quantum effect upon diffusion of light gases.

properties of a system, regardless of how closely it can be made to agree with some, especially if there are adjustable parameters. A model that is consistent with all of the pertinent properties, even if only approximately, probably can be refined to become more precise; but if it is in irreconcilable conflict with any part of the evidence, it is destined to be discarded, and in the meantime predictions and extrapolations based upon it should be regarded as unreliable.

I close with the most recent of our efforts to find order in what, at first, presented little but chaos. I returned recently to the study of diffusion, a subject concerning which theorizing has outstripped critical experimentation. This time I adopted gases as diffusing solutes. They offer two major advantages: first, their properties vary over the enormous range from helium to sulfur hexafluoride, a 10-fold range in molecular volume and a 20-fold range in attractive potential; and second, they lend themselves to an absolute, steady-state method of experimentation.

The diaphragm used by Marvin Ross (*26*) and later by Eva M. Voight was a stainless steel plate 1 centimeter thick and 8 centimeters in diameter. It was bored with 255 holes 1 millimeter in diameter. A later diaphragm, used by K. Nakanishi (*27*), consisted of 2962 pieces of stainless steel hypodermic tubing imbedded parallel in solder and supported by a bronze disk. It was 9.0 millimeters thick and had a total diffusion area of 5.71 square centimeters.

We determined diffusion coefficients of various gases in two liquids: carbon tetrachloride and perfluorotributyl amine, $(C_4F_9)_3N$, two liquids very different in viscosity, molecular size, cohesion, and degree of expansion.

Table 3 shows the product of the diffusion coefficients in carbon tetrachloride and the square of the molecular diameters of the gases. The virtual uniformity of this product for all gases except He, H_2, and D_2 indicates that in one solvent and at the same temperature the cross sections of the molecules largely determine their diffusivity. It is striking that this is also true for the self-diffusion of carbon tetrachloride. Other conceivable factors, such as masses and attractive potentials, are negligible.

But what about He, H_2, and D_2? John Walkley a few years earlier had found some evidence of a quantum effect in that H_2 dissolved in benzene occupies a volume larger by 8 percent than that required by D_2. We thought, naturally, that we should include He in our studies, and also add another solvent, the fluoroamine, in which these gases are more soluble.

Table 3. Diffusion coefficients in CCl_4 times cross sections of molecules: $10^{21}D_\sigma{}^2$.

Solute	Value	Solute	Value
CCl_4	46	N_2	47
SF_6	43	CH_4	43
CF_4	45	D_2	67
Ar	43	H_2	86
O_2	45	He	~132

The results are shown in Fig. 12, where $D\sigma^2$ is plotted against the square of a parameter devised by de Boer as a measure of quantum effects. You see that the points fall on two straight lines within the limits of error of the measurements. Now nothing delights a scientist more than to be able to place his experimental points on a straight line. Plato said that the heavenly bodies must move in circles, because the circle is the most perfect geometrical figure. Well, he was wrong; it is a straight line that gives the greatest esthetic satisfaction to a scientist.

But what is the physical significance of these beautiful lines? We are accustomed to large quantum effects at low temperatures, as when dealing with liquid helium or liquid hydrogen, but not at 25°C. However, hydrogen in carbon tetrachloride is compressed by an internal pressure of 3350 atmospheres into a volume nearly as small as its volume as liquid at its boiling point, and it acquires what is known as "zero-point energy," well in excess of its classical energy. According to the Heisenberg uncertainty principle, it is not possible to fix absolutely both the position and the momentum of a particle; they are subject to joint uncertainties whose product is the Planck constant, *h*. The square of the de Boer quantum parameter of a gas is a measure of the Heisenberg uncertainty in energy and may be thought of as the ratio of zero-point energy to classical energy. The internal energy of the fluoroamine is much less than that of carbon tetrachloride (2170 atmospheres as opposed to 3350 atmospheres); hydrogen molecules dissolved in it are not squeezed into nearly as small a volume (54 as opposed to 38 cubic centimeters per mole), and its zero-point energy is correspondingly smaller.

The successive stages in these diffusion studies are typical of how a scientist, in exploring a certain area, may hit upon something unexpected and exciting, and then, when he has finished with that region, his curiosity is aroused by another just beyond.

Last year, while attending the science fair in Albuquerque, I was a luncheon guest at a country club. I met there a genial, retired gentleman. He expressed astonishment at hearing that I am still carrying on research. "Why don't you go fishing?" he said. I tried, I fear in vain, to convince him that I was having more fun fishing than he was. I was doing my fishing in a laboratory. The fish I catch vary in size; some are small, some medium, some larger, like the beautiful straight lines in Fig. 12. I expect to continue my fishing as long as competent young scientists are willing to work with me, NSF is willing to pay expenses, my university will provide laboratory space and facilities, and editors are willing to publish what we produce. I close with this advice to ambitious young scientists: fish for fun, not for the market, not to beat a record.

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