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Physical Science Section

THE SOLUBILITY OF ANTHRACENE AND PHENANTHRENE IN VARIOUS SOLVENTS AS A FUNCTION OF TEMPERATURE

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In order to discuss our experimental results it is necessary to introduce two concepts — that of the *ideal* solution and of the *regular* solution. In order to understand the meaning of the *ideal* solution it is probably well to think first of a pure liquid at constant temperature in equilibrium with its vapor. The molecules of the liquid are conceived to be in completely random and chaotic movement, and the vapor pressure of the molecules over the liquid is constant and characteristic of the liquid for each particular temperature. If, now, to this pure liquid is added another molecular species, the original liquid is diluted, and the fraction of the total number of molecules due to the original substance is reduced from 1 (100%) to a fraction less than 1 (100%). Consequently, the vapor pressure of the original liquid is reduced. If the molecules of the original substance enjoyed completely random distribution within the original liquid, and if the added molecules do not disturb this randomness in any way; that is, if the nature of the forces surrounding the original molecules is not changed by the added molecules; then the effect of the addition is simply one of dilution of the original molecules. We can think of them under these simplifying circumstances as not caring whether they are surrounded by molecules of their own kind or molecules of the other kind, and it seems reasonable to believe on this basis that the vapor pressure of the original liquid will be reduced to the same extent that the fraction of the original kind of molecules is reduced. For example, suppose we have a pure liquid with a vapor pressure of 40.0 mm. at some temperature. The fraction of these molecules present is 1 or 100%. Let us add to this liquid sufficient molecules of another kind of substance to lower the fraction of the original molecules to 0.9 or 90%. Thus, if the added molecules do not change the intermolecular forces in any way, we would expect that the vapor pressure of the original molecules in equilibrium with the solution would be reduced to 0.9 of 40 mm. or 36 mm. This is Raoult's law, which is taken as the definition of the ideal solution, at constant temperature. This is expressed mathematically by the equation

$$P_1 = P_1^\circ \times N_1$$

where P_1 is the vapor pressure of component "1" above the solution, P_1° is the vapor pressure of pure liquid "1" at the temperature, and

N_1 is its mole fraction in the solution. This equation can evidently be written for each constituent of a solution which is ideal. If the added solute is a solid, P^o refers to the vapor pressure of the supercooled liquid at the temperature in question. If account is taken of the variation of P and P^o with temperature, an equation is obtained which might be regarded as Raoult's law for changing temperature. This equation is

$$\log N_2 = \frac{\Delta H_f}{4.57}\left(\frac{1}{T_m} - \frac{1}{T}\right),$$

where N_2 is the solubility of the solute expressed in mole fraction, ΔH_f is the heat of fusion, T_m is the melting point, and T the temperature at which the solubility is being measured. This equation represents the variation with temperature of the solubility of a solid solute. It shows us that the logarithm of the mole fraction of the solute in its saturated solution is a linear function of the absolute temperature. The slope is equal to $\frac{\Delta H_f}{4.57}$. We can thus calculate the ideal solubility of any solid if we know its heat of fusion and its melting point. It is important to notice that this ideal equation of solubility involves only properties of the solute and none of the solvent. The interpretation of this is, of course, that the solubility of a given solid is the same at a particular temperature in any solvent with which it forms ideal solutions. The conditions which must obtain in order that substances form ideal solutions have been mentioned only very casually. They are:

(a) No compound formation between solute and solvent.
(b) No association of molecules due to dipoles.
(c) Complete randomness of distribution of the molecules in the solution.

It can be shown by thermodynamics that there is another condition which must obtain in order that two substances form ideal solutions at all temperatures and pressures. This is that the solvent and solute have identical values of a property known as *internal pressure*. The equality of internal pressures is a necessary condition for ideality, but not sufficient, for conditions (a), (b) and (c) must also hold if the solution is to obey Raoult's law at all temperatures and pressures. The internal pressure of a liquid is a measure of the intermolecular forces in that liquid. Liquids in which the molecules exert a strong force of attraction upon each other have high internal pressures, and conversely. For example, in methanol, a highly polar liquid, the forces of attraction between the polar molecules bestows a very high internal pressure upon methanol. On the other hand, non-polar liquids, in which the forces of attraction between the molecules of the liquid are relatively small, have lower internal pressures; i.e., liquid helium, where the forces between the atoms are small, has a very low internal pressure. In case the solute in a solution is a solid, the internal pressure refers to that of the supercooled liquid.

We will find it very convenient to talk about the properties of the supercooled, molten solute, because the process of dissolving may be thought of as broken up into two steps; first, the fusion of the solid, and second, the mixing of the molten solute with the liquid solvent. Because of this, the total heat of solution of a solid in its saturated solution may be considered as the sum of the heat of fusion of the solid and the heat of mixing of the two liquids. In ideal solutions, because of the complete indifference of the two species of molecules to each others' presence, the heat of mixing must be zero, and therefore, in ideal solutions, the heat of solution is equal to the heat of fusion of the solid solute.

However, we do not live in an ideal universe, and most of the solutions with which we have to deal are not ideal solutions. In fact, cases of solutions which obey Raoult's law at all temperatures and pressures are the exceptions rather than the rule. The ideal solution is something which is approached to a greater or lesser degree by real solutions. It has become convenient to conceive of a class of solutions in which the first three conditions already mentioned hold, i. e., in which there is no compound formation, no association due to dipoles, and where the molecular distribution is completely chaotic, but where the internal pressures of solvent and solute are not equal. These solutions are called *regular* solutions by Hildebrand. They differ from ideal solutions only to the extent that the internal pressures of solvent and solute differ from each other.

Since the only difference between regular solutions and ideal solutions is that the internal pressures of solvent and solute are not equal, it seems reasonable to suppose that the extent to which they deviate from ideality will depend upon the extent to which the internal pressures differ. Applying this to the problem of solubility, it would follow that the extent to which the solubility of a solute deviates from its ideal solubility will depend primarily upon the magnitude of the difference between the internal pressures of solvent and supercooled solute.

This is the starting point for Hildebrand's internal pressure theory. Upon the basis of a few bold assumptions and sweeping simplifications, he has derived equations for the extent of deviation from ideality of the class of regular solutions. The extent of this deviation depends upon the differences in internal pressures of solvent and solute.

There are two principal equations in Hildebrand's theory. The simpler of the two is that which obtains when the molar volumes of solvent and supercooled solute are identical. This is

$$\mathrm{RT}\ln \frac{N_2{}^{i}}{N_2} = N_1{}^2 \left[(E_1)^{1/2} - (E_2)^{1/2}\right]^2,$$

where $N_2{}^{i}$ is the ideal solubility as calculated from the Raoult equation for changing temperature, N_2 is the actual solubility, N_1 is the mole fraction of the solvent, and E_1 and E_2 are energies of vaporization of solvent and solute respectively. It can be seen that the greater the difference in energies of vaporization, and hence in internal pressures, the greater will be the deviation from ideality. Since both factors on the right side of the equation are squared, $\ln N_2^i/N_2$ will always be positive, and therefore the actual solubility will always be less than the ideal solubility.

The assumptions made by Hildebrand in deriving these equations were the following:

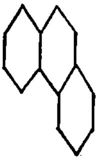
1. The molecules of solvent and solute are spherical and follow a distribution characteristic of spheres.
2. The forces of attraction between non-polar molecules are inversely proportional to the sixth power of their distance apart, or
$$E = -k/r^6.$$
3. The proportionality constant for the attraction between unlike molecules is the geometric mean of the force constants between like molecules. Thus, if for species "1" we have
$$E_{11} = -k_{11}/r^6,$$
and for species "2" we have
$$E_{22} = -k_{22}/r^6,$$
it is assumed that
$$E_{12} = -(k_{11} \cdot k_{22})^{1/2}/r^6,$$
since
$$k_{12} = (k_{11} \cdot k_{22})^{1/2}.$$

Another equation, of more general application, is for the case where molar volumes of solvent and liquid solute are not equal:

$$RT\ln\frac{N_2^i}{N_2} = V_1^2 v_2\left[\left(\frac{E_1}{v_1}\right)^{1/2} - \left(\frac{E_2}{v_2}\right)^{1/2}\right]^2$$

We are interested in the solubility of the two structural isomers, anthracene and phenanthrene, both non-polar compounds, in non-polar solvents because we can expect that such solutions will belong to the class of regular solutions. A study of the regular solutions of anthracene and phenanthrene seems important also because any such study is a study of the assumptions on which the internal pressure theory of solubility is based, and is therefore an indirect study of the liquid state. Of the three states of matter, the gaseous, liquid and solid states, the liquid state is the least understood. Evidently it shares some of the disorder of the gaseous state with some of the order characterizing the solid state. Also, any differences between the behavior of anthracene and phenanthrene may be attributed to the difference in their structure. And finally, because of the fact that phenanthrene is a parent substance for the cancer-producing hydrocarbons, a study of its properties may some day be of use to workers in other fields.

Following is a table of some of the important physical properties of anthracene and phenanthrene.

	Phenanthrene	Anthracene
Structural formula		
Melting point	99.5° C.	218.0° C.
Heat of fusion (kg. cal./mole)	4.45	6.89
Energy of vaporization (kg. cal./mole)	13.6	14.0

From the small difference between the energies of vaporization of anthracene and phenanthrene, one would predict that the internal pressures of the two isomers were nearly identical, and on the basis of internal pressures alone that both would deviate from ideality to approximately the same extent.

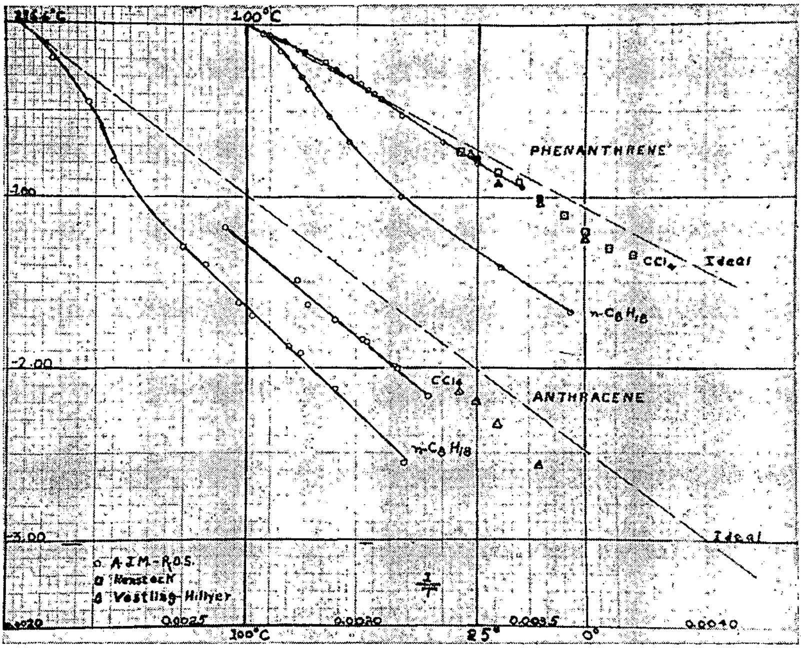
Discussion of Results

The method of measuring solubility was the so-called "synthetic" method, in which weighed quantities of solvent and solute are sealed up together in glass tubes about 12 mm. in diameter, which are placed in a bath. The tubes are rocked, and the temperature of the bath is raised slowly until the last particle of solid just goes into solution. This is the lowest temperature at which solvent and solute are completely miscible. At this temperature the solubility of the solute in its saturated solution is given by its mole fraction in the tube.

The principal advantage of the synthetic method over the analytic method is the much greater range of temperature which it allows. Temperatures greatly exceeding the normal boiling point of the solvent can be attained with the use of a suitable liquid in the bath. The medium used in the bath was water for temperatures up to 100°, and paraffin for temperatures from 100° to 197°, that being the highest temperature at which solubility was measured. The chief disadvantage of the method lies in the difficulty of assuring the attainment of equilibrium throughout the tube at all times, since any local differences in temperature might cause too high or possibly too low a solubility temperature.

Graph

The accompanying graph was made by plotting log N_2 against $1/T$. According to the Raoult equation for changing temperature, this should give a straight line if the molar heat of fusion is constant, which is, of course, only approximately true. These "ideal" solubilities are represented by the dotted lines on the graph. Thus one would expect anthracene to be less soluble at any temperature than phenanthrene, both because of its higher heat of fusion and its higher melting point. It can be seen that the slope of the ideal curve of phenanthrene is less than that of anthracene, since the slope is equal to $-\Delta H_f/4.57$.



It is apparent from the graphs that the actual solubility is less in all cases than the ideal solubility, as was predicted from the internal pressure theory, but the deviation becomes less at the temperature rises. Qualitatively, one can see that the solubility should approach ideality at higher temperatures because at the higher temperatures the intermolecular forces become less important in comparison with the increasing kinetic energy. The temperature at which a given real solution will become ideal cannot as yet be predicted. It can be seen that the curves for the solubility of both isomers in carbon tetrachloride becomes ideal at lower temperatures than the curves for solubility in n-octane.

In both cases the solubility in octane is further from ideal than the solubility in carbon tetrachloride. This is in qualitative agreement with the predictions of the Hildebrand internal pressure theory, because the internal pressures increase as we go from n-octane to carbon tetrachloride to phenanthrene to anthracene, and since the difference in internal pressures between n-octane and solute is greater than between carbon tetrachloride and solute, we expect the deviation from ideality in octane to be greater. To give some idea as to the magnitude of internal pressures in non-polar liquids, the internal pressure of n-octane is about 2000 atmospheres/cm^2, and for super-cooled phenanthrene (liquid) at 25° it is 3550 atmospheres/cm^2.

The data of Henstock and of Hillyer and Vestling were all made by the analytic method, and they check reasonably well with the data obtained by the synthetic method. The synthetic method was checked by the writers for the solubility of phenanthrene in carbon tetrachloride at 25° by the analytic method, and the results were in very close agreement.

Carbon tetrachloride was chosen as solvent because its molecule is very nearly a perfectly spherical molecule as well as non-polar, and therefore it would apparently satisfy the requirements of regular solutions. N-octane was chosen because its molar volume is very close to that of liquid phenanthrene, n-octane having a molar volume of 158 cc., and phenanthrene 163 cc. at 25°. Also, no measurements of solubility in octane have been made before, and therefore the data are increasingly important.

* * *

STRUCTURAL GEOLOGY AT LLALLAGUA, BOLIVIA

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Location

Llallagua is located about 75 kilometers southeast of Oruro, Bolivia near the center of the Bolivian "Tin Belt." This "Tin Belt" is an area 800 kilometers long and 150 kilometers wide. It is situated where the axis of the eastern range of the Andes turns from northwest-southeast to north-south. (see fig. 1)

General Geologic Setting

In the northern part of the belt the tin ores are associated with monzonitic batholiths which intrude the Paleozoic and later sedimentary rocks. In the southern two thirds of the area the deposits are in and near quartz-latite and dacite volcanic necks and dikes. It has been shown by chemical and microscopic analyses that these different igneous rocks quite probably belong to the same magmatic province.

The northern tin deposits are of the "normal" cassiterite vein type, i. e., of hypothermal origin, associated with granitic rocks which have been greisenized near the lodes. The deposits in and near the volcanic necks are unusual when compared with most of