and sixteen oxygen atoms in the following positions of the space group D_{4h}^{13}:

8Se in 8*h* with $x = 0.133$ and $y = 0.207$
$8O_I$ in 8*g* with $x = 0.358$
and $8O_{II}$ in 8*h* $= 0.425$ and $y = 0.320$

The structure consists of chains of alternating selenium and oxygen atoms along the *c*-axis, with oxygen of a second kind bonded to each selenium atom. The observed separations are 1.78 ± 0.03 Å. for Se–O_I and 1.73 ± 0.08 Å. for Se–O_{II} with bond angles of 98 ± 2° for O_I–Se–O_{II}, 90° ± 30′ for O_I–Se–O_I and 125° ± 30′ for Se–O_I–Se.

LOS ANGELES, CALIF. RECEIVED FEBRUARY 17, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Validity of Raoult's Law for Paraffin Molecules of Very Different Length

BY JOEL H. HILDEBRAND

An interesting and fundamental question was raised during the recent symposium of the Faraday Society by Guggenheim,[1] who pointed out that the ordinarily accepted validity of Raoult's law for solutions whose components possess equal molecular fields has no sure foundation in statistical mechanics except for cases which correspond to the simple model in which molecules are spherical and "sufficiently alike so that each molecule of either species is directly surrounded by the same number of other molecules. Up to the present no one has succeeded in applying statistical mechanics to a more general model." In the discussion which followed the presentation of this paper the writer called attention to various pieces of experimental evidence indicating that the effect, if it exists, is probably a small one, as indeed the formulation by Guggenheim indicated; nevertheless, the modern treatment of solutions on the basis of their deviations from Raoult's law makes the theoretical support of this law a matter of considerable importance. The purpose of this paper is to follow up a suggestion, made during the discussion, of a model which does lend itself to statistical treatment and which, fortunately, corresponds to the actual solutions most appropriate for experimental tests of the matter: those of normal paraffins of different molecular weight. These furnish, moreover, the cases likely to be of greatest practical importance.

Our model will consist of two molecular species of identical cross section but different lengths, close-packed with their axes parallel. The longer paraffin chains are evidently parallel in the solid state and are probably not much disturbed from a similar "cybotactic" grouping in the liquid state.[2] Furthermore, the field strength of such molecules is surely the same function of the distance from the axis, *e. g.*, to separate a decane molecule from another decane molecule, parallel and in "contact," requires the same energy as to separate it from two pentane molecules, except for a slight effect due to the ends, which becomes proportionally still less for longer chains. The intermolecular distances are not strictly the same for the longer and the shorter molecules at the same temperature, for the latter possess a greater amplitude of motion for the same thermal energy. This difference, however, can be minimized by using longer molecules or lower temperatures. This point will be evident from the lower curve in Fig. 1, where the heat of vaporization per gram, $\Delta H/m$, is plotted against the temperature. The values are all evidently asymptotic to a common line as temperature is lowered. The divergence appears to be almost entirely due to more rapid expansion for the lighter species with rising temperature, as shown by the upper curve in Fig. 1, in which $V\Delta E/m^2$ is plotted against temperature, where V is the molal volume, ΔE, the molal energy of vaporization and m, the molecular weight. This is equivalent to the product of the volume and heat of vaporization per gram. The departures from a common line appear to be within the experimental errors.

Raoult's law is most often written in the form $p_1 = p_1^0 N_1$, where p_1 is the partial vapor pressure of one component, p_1^0 its vapor pressure in the pure liquid state and N_1 its mole fraction. For the present purpose we shall substitute fugacity, f, for vapor pressure. Raoult's law is then

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[1] E. A. Guggenheim, *Trans. Faraday Soc.*, **33**, 151 (1937).

[2] G. W. Stewart, *Phys. Rev.*, **31**, 174 (1928); A. Müller, *Trans. Faraday Soc.*, **29**, 990 (1933); R. Rigamonti, *Gazz. chim. ital.*, **66**, 174 (1936).

$f_1 = f_1^0 N_1$. Raoult's law follows from simple statistical considerations in the case of two molecular species of identical size and field, but not for species of unequal field and not obviously for those of unequal size. It might seem, offhand, that the fugacity of a hydrocarbon molecule should be proportional to its volume concentration, *i. e.*, $f = kn/V$, since it is under the same constraints regardless of whether its neighbors are a certain number of, say, decane molecules or half as many eicosane molecules, which would correspond to a very different mole fraction. I have already shown,[3] however, by the aid of the Gibbs–Duhem equation, that the volume concentration can be proportional to fugacity only in the special case that the molal volumes of the components are identical, in which case the above expression reduces to Raoult's law with fugacity proportional throughout to the mole fraction. This does not, of course, prove that the fugacity may not be proportional to some other function of the composition of the solution.

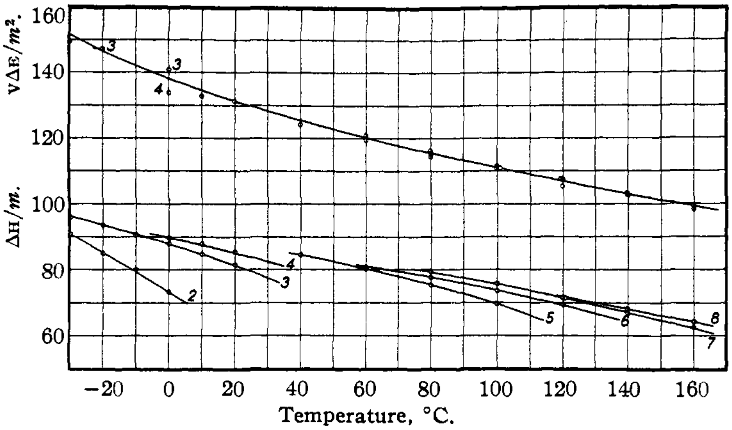

Fig. 1.—Effect of temperature and length of chain for paraffins upon the heat of vaporization per gram and upon the product of this by the specific volume of the liquid.

We may write Raoult's law in the form, $\bar{F}_1 - F_1^0 = RT \ln N$, where $\bar{F}_1$ is the partial molal free energy and F_1^0 the molal free energy in the pure liquid state. We will split up the free energy according to the general thermodynamic relation, $F = E + pV - TS$, giving

$$\bar{F}_1 - F_1^0 = RT \ln N_1 = \bar{E}_1 - E_1^0 + p(\bar{V}_1 - V_1^0) - T(\bar{S}_1 - S_1^0)$$

Since we are restricting the case to that in which there is no total energy change on transferring the component from the pure liquid to the solution, we set $\bar{E}_1 - E_1^0 = 0$. The next term on the right-hand side is at best small. For example, if we set $\bar{V}_1 - \bar{V}_1 = 3$ cc., when $N_1 = 0$, the order of magnitude seldom exceeded, the term $p(\bar{V}_1 - V_1)$ has a maximum value of about 0.07 cal., a quite negligible quantity. Our problem is then to show that, for our model, $-R \ln N_1 = \bar{S}_1 - S_1^0$.

If we follow the analysis of Stern,[4] for the entropy of a solid solution, we can regard the entropy of a lattice as made up, first, of a term due to the difference in specific heat of the molecules in the solution and in the pure substance, and, second, of a term depending upon the number of configurations which the lattice might assume. In the ordinary lattice the number of positions which molecules can occupy is regarded as fixed, and the different configurations are reckoned from the number of different possible arrangements. If the numbers of molecules of the respective species are N_1 and N_2, the total number of lattice positions is $N_1 + N_2$ and the total number of arrangements is $(N_1 + N_2)!$. However, all molecules of one species are alike, hence $N_1!$ are alike and $N_2!$ are alike. The number of different arrangements is then $(N_1 + N_2)!/N_1!N_2!$. In the pure crystal there is only one ($=N_1!/N_1!$) arrangement. The entropy of the mixed crystal is then

$$k \ln \frac{(N_1 + N_2)!}{N_1!N_2!} - k \ln \frac{N_1!}{N_1!} - k \ln \frac{N_2!}{N_2!} = k \ln (N_1 + N_2)! - k \ln N_1! - k \ln N_2!$$

Applying Stirling's formula gives

$$k(N_1 + N_2) \ln (N_1 + N_2) - kN_1 \ln N_1 - kN_2 \ln N_2$$

Differentiating with respect to N_1 at constant N_2 gives $k \ln (N_1 + N_2) - k \ln N_1$. Since the numbers of moles of the components are, respectively, $n_1 = N_1/N$ and $n_2 = N_2/N$ where N is Avogadro's number, we get for the transfer of a mole of component one from the pure state to the solution,

$$\bar{S}_1 - S_1^0 = -R \ln \frac{n_1}{n_1 + n_2} = -R \ln N_1$$

In our model of a solution of paraffins, the specific heat term must be practically negligible, hence the entropy must depend mainly upon the possible configurations. It has been customary to calculate the number of configurations as above, with reference to a definite lattice

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(3) J. H. Hildebrand, *Chem. Rev.*, **18**, 315 (1936).

(4) O. Stern, *Ann. Physik*, [4] **49**, 823 (1916); **51**, 237 (1916); *cf.* also, K. F. Herzfeld, *Z. Physik*, **16**, 84 (1923).

of points representing the mean positions of the atoms. This has made it necessary to limit consideration to species so nearly alike in size and shape that a given point-lattice can serve to describe the structure. In the case of paraffins, this would require that the length of the longer chain must be an integral multiple of that of the shorter. I wish to suggest that the lattice of points is, after all, artificial, like a given set of coördinate axes, and that it should be possible to determine the number of configurations in a more general way, applicable, at least, to linear molecules of any relative lengths. I propose, therefore, that the number of configurations be determined for our model by the number of possible interchanges, sliding the intervening molecules along in the direction of their axes sufficiently to furnish the proper space for each. This is most easily seen if we arrange long and short molecules linearly, when it is evident that the number of arrangements is the same as it would be if the molecules were of equal length. We will conclude, therefore, that the above equation holds for our model as truly as for a solution whose molecules are of equal size and field strength.[5]

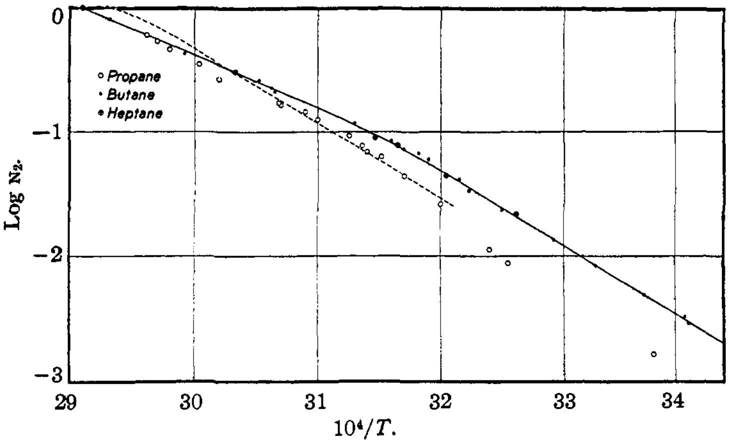

Fig. 2.—Solubility of dicetyl.

The experimental evidence at hand in confirmation of the validity of Raoult's law for solutions of straight paraffins of unequal length is at present rather fragmentary. Indeed, no extremely good agreement is to be looked for, since solutions of paraffins of nearly the same size often show departures from ideal behavior of several per cent., due either to experimental errors or to departures of the vapors from the ideal gas laws. The system investigated from among the lighter paraffins showing the most extreme variation in size is butane–heptane[6] and this obeys Raoult's law very well. Ethane dissolves in heptane almost exactly to the extent demanded by Raoult's law, according to the measurements of McDaniel;[7] however, he reports that its solubility in hexane is much less, which imposes a strain upon one's credulity. The figures for solubility at 20°, calculated to mole per cent., are as follows: ideal, 2.68; in heptane, 2.79; in hexane, 1.84.

Recently Seyer and Fordyce[8] have published solubilities of dicetyl (dotriacontane) in pentane and in heptane. I have had on hand for some time measurements, obtained by Dr. A. Wachter under my direction, of the solubility of this substance in various solvents, including one paraffin, heptane. They were not published because the solubilities in some of the solvents appeared to be larger than the ideal solubility, calculated from the melting point and the heat of fusion. This state of affairs is not known to occur except as the result of solvation, which appeared out of the question in these solutions. The data were therefore withheld pending further confirmation, either experimental or theoretical. Our figures for heptane are here given in Table I and plotted in Fig. 2 in the form of the logarithm of the mole fraction of dicetyl against $1/T$. The results of Seyer and co-workers for propane and butane are shown on the same plot.

[5] The above analysis was submitted to Professor O. Stern, whose reply is important enough to be here quoted, with his permission.

"This is certainly a very amusing problem. I am convinced you are absolutely right with respect to your result as well as with the method of calculating.

"At first, I was somewhat puzzled because I could not see how to derive your results by the van der Waals theory, but after some thinking I found the solution. Perhaps you will be interested to learn of my troubles and the solution. It is like this:

"Imagine we have in the one-dimensional case a liquid consisting of two long molecules in equilibrium with the vapor phase. Now, if we break up one of the long molecules into three small ones, we would at first sight, expect the vapor pressure of the long molecules to be one-half of the previous value; because the value of van der Waals b should not be changed by this process. But according to your theory, the vapor pressure should be one-fourth. Now the solution is this: The value of the volume, v, changes. If we call the van der Waals $(v - b)$ the 'effective volume,' then this 'effective volume' is proportional to the number of molecules in the liquid; so that the 'effective volume' for the large molecule is four times as large and the vapor pressure four times as small."

[6] G. Calingaert and L. B. Hitchcock, THIS JOURNAL, **49**, 750 (1927); *cf.* H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934); S. Young and E. C. Fortney, *J. Chem. Soc.*, **83**, 45 (1903).

[7] McDaniel, *J. Phys. Chem.*, **15**, 587 (1911).

[8] W. F. Seyer and R. Fordyce, THIS JOURNAL, **58**, 2029 (1936).

TABLE I

SOLUBILITY OF DICETYL IN *n*-HEPTANE

t, °C.	G. per 100 g.	Mole, %
28.4	4.11	0.905
29.8	4.98	1.095
34.2	8.68	1.89
35.0	10.23	2.22
39.0	20.8	4.42
43.0	36.0	7.41
44.6	44.2	8.95
56.6	198.6	30.6

The nature of the difficulty has recently come to light. It is due to a transition in the solid below the melting point which alters the form of the curve for the ideal solubility. Garner[9] and co-workers have determined the heats of transition and fusion for the normal paraffin hydrocarbons containing 22, 26, 30, 34 and 35 carbon atoms. By interpolating their results we may obtain data for dicetyl, for the molal heat of fusion of the α-form, the heat of transition α to β and the molal heat capacities of the liquid α and β forms. We may then calculate the ideal solubility curve of the α-form from its melting point down to the transition point and the ideal solubility of the β-form from there down. We cannot at present place too much confidence in the result of this calculation, however, on account of some uncertainty regarding the data. The fusion temperature of dicetyl interpolated from the data of Garner and co-workers is 68.4° while the transition temperature is 63.5°. The dicetyl used by Wachter, however, melted at 70.2°. Delcourt,[10] in Timmermans' Laboratory, has found 70° for the melting point, and Deffet[11] reports a melting point of 70.0° and a transition point of 64.3°. The material used by Seyer and Fordyce melted at 69.9°. They also give 55° for the transition temperature. It is possible that the transition between α and β is not a sharp change. Their curve for refractive index against temperature shows no sudden jump at 55° but rather a gradual rise between 55 and 70°. The data of Garner and co-workers for tetratriacontane show a rather rapid increase in the heat content of the β-form as the transition is approached and a somewhat rounded, continuous rather than sharply discontinuous change through the α to the liquid. This behavior is by no means uncommon.[12] It can be handled readily by plotting the heat content per mole of substance from some common lower temperature against $1/T$ and integrating graphically down from the melting point between this curve and the extrapolated heat content curve for the liquid, since $-\log N = (1/4.575) \int \Delta H d(1/T)$. The dotted line in Fig. 2 has been obtained in this way using data by Garner and co-workers for $C_{34}H_{70}$, multiplying by the molecular weight ratio, 450/478, and calculating equal distances below the melting points of the two substances. The curve has not been extended very far down on account of the uncertainties involved, the most serious of which is lack of knowledge concerning the change in specific heat of the liquid. The calculation must be regarded as purely tentative and will be corrected in the near future by aid of a direct calorimetric investigation of dicetyl now under way.

The ideal solubility, on the basis of this preliminary calculation, appears to be somewhat less than the observed solubility in the three solvents, although the discrepancy is not great. Most striking, however, is the agreement between the curves for butane and heptane, themselves differing considerably in length of chain. The smaller solvent power of propane is doubtless to be expected, partly, at least, on account of pressure effects not accounted for.

It is worth mentioning in this connection that the system benzene–diphenyl, which is similar in principle to the model here discussed, deviates only slightly from ideal behavior,[13] and that there are other systems composed of molecules of widely different volumes, such as sulfur, 136 cc. per mole, and iodine, 59 cc. per mole, of which this is also true. It may hardly be worth while to attempt a too close check of a pure volume effect because of the doubtful possibility of eliminating completely all differences in other factors, particularly molecular field strength.

Summary

The lattice of fixed points as a frame of reference for calculating the entropy of binary solutions is applicable only to pairs of molecular species of equal size or, at most, to molecules whose size and shape permit them to occupy a

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(9) W. E. Garner, K. van Bibber and A. M. King, *J. Chem. Soc.*, 1533 (1931).

(10) Y. Delcourt, *Bull. soc. chim. Belg.*, **40**, 284 (1931).

(11) L. Deffet, *ibid.*, **44**, 41 (1935).

(12) *Cf.* F. Simon, *Ann. Physik*, **68**, 241 (1922); W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 2193 (1928); **51**, 1441 (1929).

(13) J. C. Warner, R. C. Scheib and W. J. Svirbely, *J. Chem. Phys.*, **2**, 590 (1934).

definite number of lattice points. If a solution of long paraffin molecules is somewhat idealized as a parallel arrangement, the number of possible interchanges is the same as it would be for spherical molecules of equal size in a point lattice. This leads to the entropy and free energy of an ideal solution. The rather meager experimental evidence supports the ideal character of such solutions.

BERKELEY, CALIF. RECEIVED FEBRUARY 15, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY, INDIAN INSTITUTE OF SCIENCE]

Vapor Phase Esterification Equilibria

BY S. K. KULKARNI JATKAR AND N. G. GAJENDRAGAD

A study of various papers[1] on the vapor phase esterification of alcohols and acetic acid would seem to indicate a high temperature coefficient on the basis of Sabatiers[1e] value of 70% at 300° and Edgar's[1h] figure of 97% at 53°, but the large possible error admitted by Edgar and the lack of precision in the data of earlier workers, leaves doubt as to the actual position of equilibrium at intermediate temperatures, especially in view of the agreement of the constants found by Frolich, Carpenter and Knox[1l] at 280–300° and Swietoslawski[1i,j] at 75°. Parks and Huffman[2] have used these values in calculating the free energy of ethyl acetate, and obtained satisfactory concordance with estimates based on the third law, but in disagreement with results of other workers.

Swietoslawski and co-workers apparently did not correct for acetic acid polymerization nor for the activities of the compounds, both of which are appreciable at 75°. As to the high values of Frolich and coworkers, the only probable explanation for them is that some of the catalyst must have been in the cooler portion of their apparatus. On account of the high temperature coefficient of the equilibrium constant, the reaction products must be "frozen," and it seems probable that temperature errors may account for some of the other experimental discrepancies.

Figure 1 shows a plotting of log Kp against $1/T$ of the results of various workers, and harmonizes out all the values from 77 to 300° except those of Frolich, *et al.* The fact that a straight line can be drawn among most of the values shows that ΔC_p for this reaction is practically zero, and it is only coincidence that our values lie between those extrapolated from the results of others. The acetic acid dissociation and the compressibility corrections are too small to affect our results. Perhaps the dotted line drawn through the more accurate values of Essex and Clark represent the true position of affairs.

The object of the present work was to obtain results with silica and potassium alum catalysts and discuss them in the light of the work of other investigators.

Experimental

The previously described method[1b] was used, in which the alcohol–acid mixture is allowed to flow drop by drop into a copper tube vaporizer (not attacked by acetic acid above 180°), superheated, passed through the catalyst tube and the products condensed in a test-tube in a freezing mixture.

The silica catalysts were prepared from iron-free water glass, analyzing for an $Na_2O:SiO_2$ ratio of 1.07:1 and 30.8% of water. The silicate solution was allowed to flow dropwise into 1.5 liters of vigorously stirred dilute hydrochloric acid contained in a 4-liter beaker, until the resulting gel set and stirring was impossible. The gel was then broken up, washed well with hot distilled water and dried in various ways, the most active catalyst being produced in partial vacuum. For this catalyst the optimum temperature was 260°, and the initial and final total acids agreed well except at temperature extremes.

Esterification of Ethyl Alcohol and Acetic Acid with Silica Catalyst at 260°.—For various rates of passage the esterification limit was found to be 75% for the 1:1 mixture and 91% for the 2:1 mixture (Table I).

The equilibrium also was studied from the hydrolysis side, pure ethyl acetate being taken into the buret and ester vapor saturated with water passed through the superheater into the reaction chamber, the proportion of water being

(1) (a) Jatkar and Watson, *J. Indian Inst. Sci.*, **9A**, 71 (1926); (b) Gajendragad, Jatkar and Watson, *ibid.*, **15A**, 59 (1932); (c) Gajendragad and Jatkar, *J. Indian Chem. Soc.*, **12**, 486 (1935); (d) H. T. Briscoe and F. E. Dolian, *Proc. Indiana Acad. Sci.*, **42**, 101 (1933); *C. A.*, **27**, 5719 (1933); (e) Sabatier and Mailhe, *Compt. rend.*, **152**, 358, 494 (1911); (f) Mailhe and Godon, *Bull. Soc. Chim.*, [4] **29**, 101 (1921); (g) Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924); (h) Edgar and Schuyler, THIS JOURNAL, **46**, 64 (1924); (i) Swietoslawski and Poznanski, *Compt. rend.*, **184**, 92 (1927); (j) Swietoslawski and Salcewicz, *ibid.*, **199**, 130 (1934); (k) Gajendragad, *Proc. 15th Indian Sci. Cong.*, 148 (1928); (l) Frolich, Carpenter and Knox, THIS JOURNAL, **52**, 1565 (1930); (m) Jatkar and Gajendragad, "Proc. Indian Sci. Cong., Nagpur," 1931; (n) Tidwell and Reid, THIS JOURNAL, **53**, 4353 (1931); (o) Essex and Clark, *ibid.*, **54**, 1290 (1932).

(2) Parks and Huffman, "Free Energy of Organic Compounds." Reinhold Publishing Corporation, New York, N. Y., 1935, p. 174.