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THE THERMODYNAMIC PROPERTIES OF PARAFFIN MIXTURES. I

BY

J. N. BRØNSTED AND JØRGEN KOEFOED

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1. Introduction.

The present paper contains an investigation on some thermodynamic properties of mixtures of normal paraffins at constant temperature. It forms a continuation of previous work on the influence of the size of molecules upon their thermodynamic behaviour in solution.[1] This influence is clearly demonstrated when comparing molecules approximately identical in chemical respect and deviating from each other only regarding magnitude. Molecules of this kind have been described as "isochemical" molecules.

The normal paraffins constitute a series in which the isochemical relationship is particularly conspicuous. On the thermodynamics of these mixtures there exists only little information. The general opinion undoubtedly is to regard them as ideal or almost ideal solutions. The present investigation does not support this view. They cannot be described as perfect solutions nor do they belong to the group of so called "regular" solutions. Nevertheless they possess, in their own way, properties of a singularly simple character.

A direct and obvious method for testing the thermodynamic nature of paraffin solutions consists in determining the solubility of a solid paraffin in a series of the lower liquid homologues. In the case of ideal conditions the solubility in terms of mole fractions should remain constant, irrespective of the individuality of the liquid paraffin applied as a solvent. With the paraffin $C_{34}H_{70}$ as saturating substance and the paraffins from hexane to cetane as solvents it was shown in this laboratory already in 1938 that great deviations from ideality actually existed in these

[1] J. N. Brønsted: C. r. d. Lab. Carlsberg. **22**, 99 (1938) (with further references).

mixtures, but as the investigations in question are not yet concluded, the results are being reserved for later publication.

Another method for testing the character of the solution and for quantitatively determining their deviations from the ideal laws consists in measuring the vapour pressure of a volatile component in dependence of its concentration in the liquid mixture. It must be recognized, however, that a satisfactory utilization of this principle demands a very considerable increase in the accuracy of the experimental methods so far in existence. Furthermore the question of the deviations of the paraffin vapours from the laws of perfect gases has to be considered. The present article deals with the problem indicated from these points of view.

2. Previous Investigations.

Very few data of significance to the problem in hand can be obtained from existing literature. LESLIE and CARR[1] have determined concentration-boiling point diagrams for the systems hexane-heptane, hexane-octane, and heptane-octane, but their results are too inaccurate to be of any value for our calculations. CALINGAERT and HITCHCOCK[2] determined the volume-pressure relations in the heterogeneous vapour-liquid systems of butane-pentane, butane-heptane, and pentane-heptane, and were able from these determinations without a special analysis of the vapour to calculate the composition of the co-existing phases. In the case of butane-heptane they found conformity with the laws of perfect solutions, whereas in the two other cases the vapour pressures came out considerably below the ideal values. This result must be looked upon as subject to doubt since the butane-heptane system consists of the more dissimilar components and therefore should give the greater deviation from ideality. It must be assumed, therefore, that the accuracy of these measurements is insufficient. Also the assumption of the validity of the gas laws at the rather high pressures applied is hardly permissible. For

[1] E. H. LESLIE a. A. R. CARR: Ind. Eng. Chem. **17**, 810 (1925).

[2] G. CALINGAERT a. L. B. HITCHCOCK: J. Am. Chem. Soc. **49**, 750 (1927). Cf. also H. A. BEATTY a. G. CALINGAERT: Ind. Eng. Chem. **26**, 304 (1934), G. L. MATHESON a. L. W. T. CUMMINGS: Ibid. **25**, 724 (1943).

similar reasons the work of SAGE and LACEY[1] on propane-pentane and other mixtures is of no value for our purpose.

Of greater interest are the careful and accurate measurements by HILDEBRAND[2] of the vapour pressure in the hexane-cetane system at 25° C. In this system the vapour pressure is exerted solely by the volatile component, and the measurements for that reason lend themselves to a much simpler interpretation. By plotting the ratio of the vapour pressure p/p_0 against the mole fraction in the liquid mixture an almost straight line comes out. Or, in the words of the author, "The ratio of the vapour pressure of hexane from the solution to that from the pure liquid, p/p_0, agrees with its mole fraction N, within what is doubtless the experimental error." This result undoubtedly suggests the presence of ideal conditions in the liquid mixture of hexane and cetane. From a few measurements at lower temperatures (14° C. —23° C.) yielding the same value for p/p_0N as the measurements at 25° C. HILDEBRAND infers that also the entropy of the mixture follows Raoult's law, i. e. has the ideal value.

A close inspection of HILDEBRAND's data in the region dilute in hexane shows vapour pressures somewhat below those calculated from the straight line relationship. The method employed, however, does not permit of accurate determinations in this region. It is not surprising, therefore, that no attention is paid by the author to these small deviations, even though the region in which they seem to appear is undoubtedly the most interesting from a theoretical point of view.

The problem of the thermodynamic properties of n-paraffin mixtures from the standpoint of statistical mechanics was dealt with in a previous paper by HILDEBRAND.[3] On the assumption that the entropy in the mixture depends mainly on the possible configurations, and assuming that an idealization of the mixture as a parallel arrangement of the long paraffin molecules is permissible as an approximation, the ideal value $-R\ln x_i$ for the entropy of a paraffin component i in the mixture was derived. This again on certain simplifying assumptions leads to ideal thermodynamic properties for the mixture in general. The results

[1] B. H. SAGE a. W. N. LACEY: Ind. Eng. Chem. **32**, 442 (1940). Cf. also W. B. KAY: ibid. **30**, 459 (1938).

[2] J. HILDEBRAND: J. Phys. Chem. **43**, 109, 297 (1939).

[3] J. HILDEBRAND: J. Am. Chem. Soc. **59**, 794 (1937).

of the measurements are looked upon as a corroboration of this theory.

FOWLER and RUSHBROOKE[1] have made an attempt to extend the statistical theory of perfect solutions[2] to mixtures in which the molecules are distinctly unequal in size. They reduce the liquid arrangements to those of a simple regular lattice and represent a change of size by taking one molecule twice the other and requiring it to occupy two adjacent lattice points. Furthermore all configurations are assumed to have the same energy. On the basis of these simplifying assumptions they show that deviations from the ideal vapour pressure curves may be due to the components of the mixture differing widely in molecular size and not necessarily due to intermolecular forces.

In the paper just mentioned HILDEBRAND also refers to some solubility determinations with dicetyl as a solute and various liquid paraffins as solvents. Similar determinations are reported by SEYERS.[3] We shall, however, postpone the discussion of these measurements, which are of no great accuracy, to a subsequent communication.

3. The Deviation of Paraffin Vapour from the Ideal Gas Laws.

An imperfect gas, within small pressure intervals, may in many cases obey the following equation of state[4]:

$$p\,(v + \Delta) = RT, \qquad (1)$$

where Δ, the residual volume, is a positive constant independent of pressure, but dependent on temperature. When the ideal mole volume is v^*, Δ evidently is given by:

$$v^* - v = \Delta. \qquad (2)$$

If by μ and a, respectively, we denote the chemical potential and activity of the gas considered, we have at constant temperature:

[1] R. H. FOWLER a. G. S. RUSHBROOKE: Trans. Far. Soc. **33**, 1272 (1937).
[2] Cf. E. A. GUGGENHEIM: J. Phys. Chem. **34**, 1751 (1930), Proc. Royal Soc. A **135**, 181 (1932), **148**, 304 (1935), Trans. Far. Soc. **33**, 151 (1937).
[3] W. F. SEYERS: J. Am. Chem. Soc. **60**, 827 (1938).
[4] LEWIS a. RANDALL: Thermodynamics, 197 (1923).

$$\mu - \mu_0 = RT\ln a, \tag{3}$$

or:

$$d\mu = RTd\ln a = vdp. \tag{4}$$

By introducing (1) in (4) we get:

$$d\mu = RTd\ln a = RTd\ln p - \Delta dp, \tag{5}$$

or:

$$\mu - \mu_0 = RT\ln a = RT\ln \frac{p}{p_0} + \Delta(p_0 - p). \tag{6}$$

In this equation μ_0 is obviously the potential of the gas in a standard state in which $a = a_0 = 1$ and $p = p_0$.

Equation (6) expresses the chemical loss of work connected with the differential and isothermal transfer of one mole from p to p_0. The last term of the equation is the correction caused by the deviation of the gas from the ideal equation of state.

Measurements by S. YOUNG[1] at various temperatures gave densities of saturated hexane vapour corresponding to the following values of Δ:

t (C°)	Δ (L)
56.4	1.97
77.6	1.42
103	1.10
124.5	0.99

An uncertain extrapolation from these temperatures to 20° results in a value about 3 L for Δ. YOUNG's data, however, are hardly very exact. A greater accuracy is obtained by extrapolating with regard to ν, i. e. the number of carbon atoms in the paraffin molecule on the basis of the following more recent information.

From the data of SAGE, WEBSTER a. LACEY[2] and SAGE, SCAAFSMA a. LACEY[3], who have determined the ratio of fugacity to pressure of some normal paraffins, the expression:

$$\log \frac{a}{p} = -\alpha p + \beta, \tag{7}$$

[1] S. YOUNG: J. Chem. Soc. 1895, 1082.
[2] B. H. SAGE, D. C. WEBSTER a. W. N. LACEY: Ind. Eng. Ch. **29**, 1188 (1937).
[3] B. H. SAGE, J. G. SCAAFSMA a. W. N. LACEY: Ibid. **26**, 1218 (1934), **27**, 49 (1935).

where a stands for activity, is derived for propane, butane, and pentane at 21°.1 C. The values of a for these paraffins, which are also in conformity with DESCHNER a. BROWN's[1] measurements on propane at 30° and 50° C. and with the value found for hexane in the present investigations (see p. 15) are given in Table 1, the pressure being reckoned in cm Hg.

Table 1.

n-Paraffin	a	$\log a$	Δ
C_3H_8	$0.95 \cdot 10^{-4}$	$\bar{5}.978$	0.4
C_4H_{10}	1.67 -	$\bar{4}.223$	0.7
C_5H_{12}	2.98 -	$\bar{4}.474$	1.3
C_6H_{14}	5.0 -	$\bar{4}.699$	2.1
C_7H_{16}	8.7 -	$\bar{4}.94$	3.7

By plotting $\log a$ against v we obtain a straight line for the 4 paraffins, and an extrapolation from this line gives the a-value for heptane stated in the table. The corresponding Δ-values computed from (6) and (7) by the equation:

$$a = \frac{\Delta}{RT} \cdot \frac{0.4343}{76},$$

where R = 0.08206, and expressed in L, are also given in the table.

4. Application of Vapour Pressure Measurements for Determination of the Activity Coefficient in Solutions.

In applying equation (6) for the determination of activity and activity coefficients in the liquid mixture, we shall assume the liquid system to consist of a volatile component K_1 and a non-volatile component K_2. The activity of K_1 in the solution is defined by the equation:

$$\mu_1 - \mu_{1(1)} = RT \ln a_1, \qquad (8)$$

analogous to (3), but in contradistinction to the latter (8) is based on the presupposition of constant pressure as well as

[1] W. W. DESCHNER a. G. G. BROWN: Ibid. **32**, 840 (1940).

constant temperature. The equation includes the convention that the activity = 1 for the pure component at the given experimental conditions.

The change in a_1 due to the change of pressure is expressed by:

$$\left(\frac{\partial \ln a_1}{\partial p}\right)_T = \frac{V_1 - V_{1(1)}}{RT}. \tag{9}$$

The difference $V_1 - V_{1(1)}$ in the mixtures here considered, however, hardly exceeds $2 \cdot 10^{-3}$ L. Consequently we shall not introduce any traceable error if the terms in (8) are considered independent of pressure, and the equation is applied in the pressure intervals of the actual experiments. The potential difference in (8) may therefore be identified with the potential difference in (6), when this equation is applied to the component K_1 in states where the gaseous and liquid phases are in equilibrium with one another.

Thus for K_1 in the solution we may write:

$$\mu_1 - \mu_{1(1)} = RT \ln a_1 = RT \ln \frac{p_1}{p_{1(1)}} + \Delta (p_{1(1)} - p_1), \tag{10}$$

where p is the vapour pressure of K_1 in the solution and $p_{1(1)}$ the vapour pressure of K_1 in a pure state.

For the activity coefficient of K_1 defined by:

$$a_1 = x_1 f_1 \tag{11}$$

we thus obtain:

$$\ln f_1 = \ln \frac{p_1}{p_{1(1)} x_1} + \frac{\Delta}{RT} (p_{1(1)} - p_1), \tag{12}$$

or writing:

$$\frac{p_1}{p_{1(1)} x_1} = f_1' \tag{13}$$

where f_1' may be called the "pressure activity coefficient":

$$\ln f_1 = \ln f_1' + \frac{\Delta}{RT} (p_{1(1)} - p_1). \tag{14}$$

f_1' is the activity coefficient, calculated under the presupposition of the applicability of the gas laws to the vapour, and the last term of (14) represents the correction in $\ln f_1$ for the

existing deviations. If the correction is small, equation (14) might be written:

$$\ln f_1 = \ln f_1' + \frac{\Delta}{RT} p_{1(1)} x_2, \tag{15}$$

the correction term:

$$\frac{\Delta}{RT}(p_{1(1)} - p_1) = A \tag{16}$$

being replaced by:

$$\frac{\Delta}{RT} p_{1(1)} x_2 = B. \tag{17}$$

The difference between the 2 quantities A and B is easily obtained by means of (13) as:

$$A - B = \frac{\Delta}{RT} p_{1(1)} x_1 (1 - f_1'). \tag{18}$$

For hexane according to Table 1 $\Delta = 2.1$ L. For the mixture of hexane and cetane, as will be shown below, the following equation holds true:

$$-\log f_1' = 0.048\, x_2^2 + 0.0060\, x_2. \tag{19}$$

Thus from (17), (18), and (19) the following data of Table 2 are computed:

Table 2.

x_1	$-\log f_1'$	f_1'	A − B
0	0.054	0.8831	0
0.1	0.04428	0.9031	0.000135
0.2	0.03552	0.9215	0.000218
0.3	0.02772	0.9382	0.000257
0.4	0.02088	0.9531	0.000260
0.6	0.01008	0.9771	0.000191
0.8	0.00312	0.9928	0.000080
1.0	0	1.0	0

The error in using the simpler expression (15) instead of (14) is thus seen to be less than 0.00026 in $\log f_1'$, corresponding to 0.06 per cent. in f_1'.

The magnitude of the difference A — B for the various paraffins is mainly determined by the product $p_{1(1)}\Delta$. As the value of this product for hexane and heptane is:

$$p_{6(6)}\Delta_6 = 12.11 \cdot 2.1 = 25.43$$

$$p_{7(7)}\Delta_7 = 3.54 \cdot 3.7 = 13.10,$$

the error involved in applying the simplified equation (15) instead of the correct equation (14) to heptane is only half of that in the case of hexane.

5. Experimental Method.

The method described below is generally applicable for the determination of the relation between vapour pressure and concentration of mixtures in which one component only is volatile. With certain reservations it is also applicable to binary mixtures fulfilling the condition that the vapour pressure of one component is small as compared to that of the other. In the present investigations the method is applied to the 3 binary systems: hexane-cetane, heptane-cetane, and hexane-dodecane.

In the apparatus constructed for the measurements and illustrated in Fig. 1 the mixture was contained in a glass flask A holding about 100 ml, which was shaken mechanically in a water thermostat for establishment of the liquid-vapour equilibrium, the pressure being read from one or two manometers B and C sealed into a system of glass tubes, with which the flask was connected by a thin capillary D. A known quantity of the non-volatile component was introduced in A before sealing and freed from air by evacuation. The system of glass tubes was communicating with reservoirs E, F, and G containing the volatile component, which was freed from air by evacuation at low temperature and distilling off from one reservoir to the other. The concentration of the mixture in A was altered by distilling the volatile component between A and the reservoirs, and it was determined by direct weighing of the flask, the thermostat being emptied of water, and the rinsed and dried flask released from the clamp by which it was attached to the shaking device and suspended by means of a metal wire under the scale of a balance solidly fixed on the wall above the thermostat.

The procedure of determing the concentration of the mixture directly by weighing a container in tight connection with the manometer system is made possible by the flexibility of the

connecting capillary and is the essential feature of the method described. A further advantage of this method consists in the possibility it offers of changing the concentration of the solution at will by distilling the volatile component to and from the solution. This makes possible the detection and removal of any trace of air in the liquid and the determination of any number of corresponding concentrations and pressures with the same air-free charges of material without opening the system or otherwise admitting the atmosphere.

When cetane is used as the "non-volatile" substance, it appears from an easy calculation that the quantity which may be distilled off from the flask by this process in the course of a series of experiments covering about 20 single determinations averages 1 mg only by a total quantity of 20—30 g.

As regards further details of the method, it may be mentioned that the capillary chosen after many experiments was drawn from an 8 mm cylinder tube to an external diameter of 0.45—0.55 mm and a length of ab. 50 cm. With this capillary the sensitiveness of the balance was about 0.5 mg. A capillary of a diameter of 0.8 mm interfered with the weighing too much, and a thinner capillary would impede a rapid vapour transmission and distillation. Naturally the whole construction had to be arranged with the greatest care and fixed accurately to prevent a change in the state of tension of the capillary during the experiment. The reproduceability of the experiments, however, proved that this requirement could be complied with.

The effect of varying buoyancy of the flask used in the experiment was eliminated by placing a bulb of the same size in the other scale. The weight of the vapour above the liquid, which is necessary for the calculations, was determined from the total volume of the flask and the known densities of the vapours.

The glass construction including manometers and reservoirs for the volatile component was blown all in one piece without stopcocks. Communication between the various portions was established by mercury valves operated by means of the two air reservoirs R—R, as indicated in the figure. The reservoirs and the manometer system could be cut off from the capillary and the quartz-mercury pump P by means of the long valves H and I, thereby making it possible to admit the atmosphere to

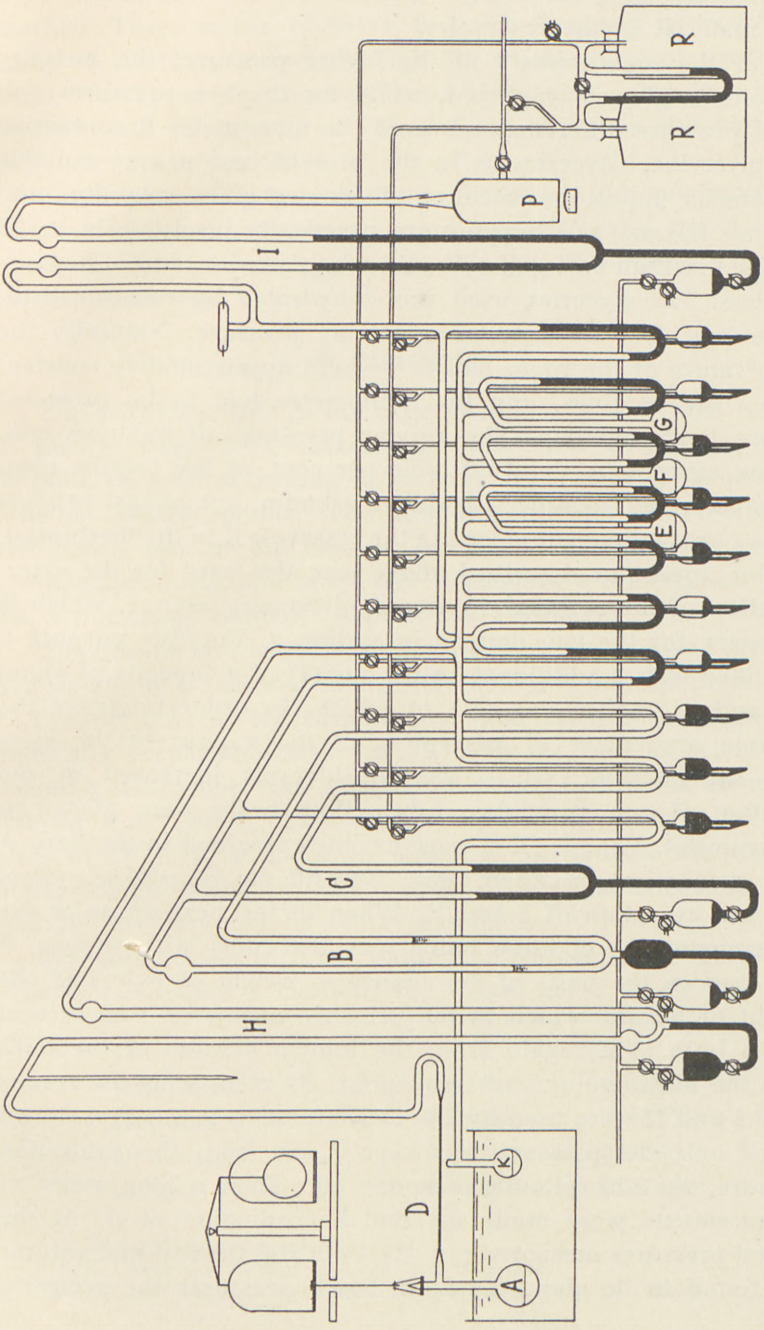

Fig. 1.

A when changing the charges without contamination of the air-free material in the reservoirs.

For the measurement of the higher pressures the mercury manometer C was employed, while for the low pressures and small pressure differences we used the manometer B containing dry glycerine. Glycerine is in the present case a very suitable manometer liquid on account of its negligible volatility, and because hexane and heptane are practically insoluble in it. Of hexane less than 0.01 g dissolves in 1 kg glycerine, and of heptane still less. The glycerine used was dehydrated by vacuum distillation and had no detectable vapour pressure. Naturally the temperature of the room had to be kept approximately constant during the readings, and the manometer had to be protected against heat radiation. The vapour pressures of mixtures containing more than about 80 mole per cent. of the volatile component were not measured against a vacuum, but against vapours of the pure component placed in the reservoir K in the thermostat.

The apparatus described above was also used for the determination of the residual volume Δ of hexane vapour, which is necessary for the calculations in section 3. For this purpose it was fitted with 2 additional bulbs, one (I) of a capacity of about 2 L and a smaller one (II) in which—in order to detect the possible occurrence of adsorption of the vapour to the glass wall—the internal surface was considerably increased by the insertion of numerous glass tubes. Both bulbs were placed in a thermostat. Vapour from pure hexane contained in the flask A after evacuation was then allowed to fill the remaining system with the exception of I and II. When in the next phase of the experiments one of these bulbs was also filled with vapour, it was easy on the basis of the change in weight of A to find the weight of hexane which at the pressure measured was present in the bulb. This again from the known volume of the bulb gives the molar volume of the vapour. By comparing the results when I and II were used for the measurements it was first shown that if only the pressure was kept $^1/_4$ cm from the saturation pressure, no adsorption was noticeable. Then a long series of measurements were made for the determination of Δ. At the highest pressures measured (10—11.7 cm Hg) the residual volume was found to be about 2.1 L, at lower pressures the accuracy

is of course smaller, and the spreading of the values was more marked. There seems, however, to be good reason to accept the value of 2.1 L as correct through the whole range of pressures from 0 to 12 cm Hg. As mentioned above this value is in conformity with the results of calculations made on the basis of previous measurements.

For heptane vapour the above method is too uncertain on account of the much lower vapour pressure, and the Δ-value stated in Table 1 was applied to this paraffin without further experimental test.

6. Materials.

The paraffins used in the experiments were of a high degree of purity. They were obtained by fractional distillation in a 60-plate column according to A. KLIT[1] and showed completely constant boiling points. The raw material for the fractional distillation was in the case of hexane, dodecane, and cetane synthetic products, and in the case of heptane a preparation from TH. SCHUCHARDT named "Heptan aus Petroleum".

The hexane and heptane preparations by progressive evaporation at 20°.00 C. showed completely constant vapour pressures, 12.11 and 3.54 cm Hg respectively. The melting point of the dodecane preparation was —9°.75 C. In the case of cetane the coloumn distillation was carried out at a pressure of about 15 mm Hg and 150° C. The sample showed a constant melting point of 18°.15 C. P. C. CAREY and J. C. SMITH[2] give the melting point of pure cetane as 18°.13, while melting points between 16° and 20° are reported by other investigators.[3]

For the density d_4^{20} we found the values given below in column 1. Column 2 contains the values given by EGLOFF.[3]

	1	2
Hexane	0.65940	0.65942
Heptane	0.68389	0.68375
Dodecane	0.74933	0.7493
Cetane	0.77340	0.77499

[1] A. KLIT: Theses, Copenhagen 1943.
[2] P. C. CAREY a. J. C. SMITH: J. Ch. Soc. 1933, 346.
[3] G. EGLOFF: Physical Constants of Hydrocarbons, p. 95 (1939).

7. Experimental Results.

Hexane-Cetane. Following some measurements more in the nature of an orientation, four independent series of determinations were carried out, the results of which are given in Table 3.

The 2nd column, headed g_{16}, contains the weight of cetane in grammes corrected for dissolved air, ab. 0.2 mg/g cetane. Column 3 contains the weight of hexane vapour, g_V, calculated

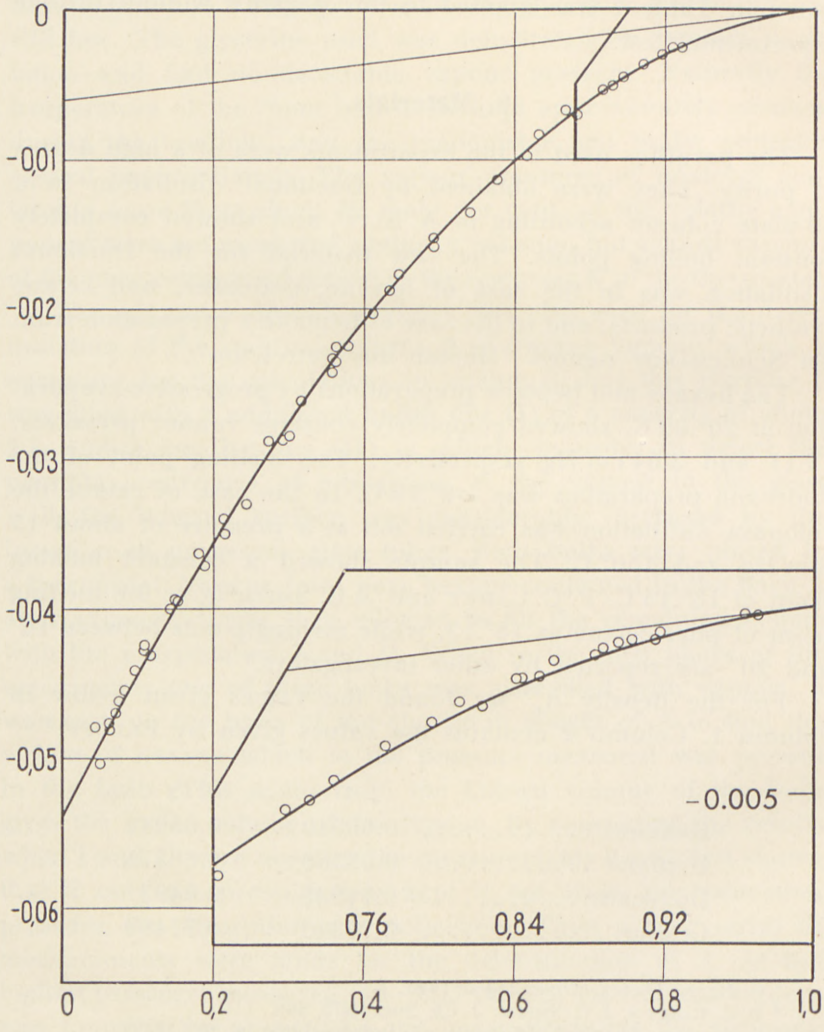

Fig. 2. Hexane-Cetane. Log f'_6 against x_6.

Table 3.

Series	g_{16}	g_V	g_6	x_6	p_6 (Hg)	p_6 (Gl)	log f'_6
					p		
2	29.219	0.0116	6.7634	0.3781	4.36		$\bar{1}$.9774
		.0070	3.0080	.2129		25.79	.9660
		.0059	2.4396	.1799		21.68	.9637
		.0050	1.9905	.1518		18.16	.9605
		.0026	0.9024	.0751		8.84	.9538
					$p_0 - p$		
3	1.2844	.0469	2.2673	.8226		23.89	.9973$_5$
		.0456	1.9044	.7958		27.50	.9969
		.0443	1.6440	.7708		30.81	.9963
		.0427	1.4232	.7443		34.52	.9954
		.0413	1.2447	.7181		38.10	.9946
		.0392	1.0498	.6823		43.08	.9928
		.0480	2.6482	.8442		20.89	.9981
		.0444	15.5584	.9695		4.05	.9998
		.0464	12.9538	.9636		4 82	.9998
		.0499	5.3001	.9156		11.30	.9991
		.0500	4.5389	.9028		12.97	.9991
		.0496	3.8534	.8874		15.04	.9989
		.0489	2.9098	.8542		19.32	.9981$_5$
		.0478	2.5995	.8418		21.21	.9981
		.0468	2.2288	.8202		24.13	.9977
		.0501	5.4667	.9179		10.93	.9993
		.0499	4.2846	.8976		13.67	.9991
		.0494	3.7031	.8834		15.62	.9987
		.0487	3.0268	.8610		18.58	.9986
		.0464	2.1011	.8114		25.34	.9975
		.0421	1.3285	.7309		36.36	.9948$_5$
		.0386	0.9881	.6675		44.70	.9933
					p		
4	14.4027	.0120	2.0466	.2718		33.33	.9712
		.0138	2.5322	.3159		38.97	.9738
		.0158	3.1060	.3617		44.86	.9763
					4.17		.9774
		.0187	4.1967	.4336	5.04		.9812
		.0208	5.2876	.4910	5.76		.9847
		.0252	9.3498	.6305	7.51		.9917
		.0247	8.7906	.6160	7.31		.9902
		.0237	7.4604	.5765	6.82		.9886

Table 3 (continued).

Series	g_{16}	g_V	g_6	x_6	p_6 (Hg)	p_6 (Gl)	log f'_6
					p		
4	14.4027	0.0225	6.4185	0.5394	6.35		$\bar{1}$.9863
		.0222	5.2836	.4908	5.75		.9841
		.0192	4.4149	.4462	5.20		.9823
		.0181	3.8182	.4106	4.76		.9796
		.0155	3.0487	.3575	4.11		.9766
						44.26	.9756
		.0128	2.2520	.2912		35.70	.9712
		.0090	1.4967	.2145		25.92	.9649
		.0065	0.9577	.1487		17.80	.9607
		.0047	0.6639	.1080		12.84	.9576
		.0031	0.4172	.0707		8.31_5	.9530
		.0027	0.3673	.0628		7.36_5	.9519
		.0047	0.6544	.1068		12.68	.9572
		.0022	0.2924	.0505		5.91	.9496
5	23.7470	.0023	0.5940	.0617		7.24	.9523
		.0031	0.8038	.0817		9.64	.9545
		.0043	1.1813	.1156		13.72	.9569
		.0052	1.4935	.1418		16.95	.9600
		.0067	2.0938	.1881		22.62	.9628
		.0098	2.8964	.2428		29.47	.9669
		.0124	3.8728	.3000		36.80	.9714
		.0036	0.9389	.0941		11.14	.9559

from the pressure. Column 4 gives the weight g_6 of hexane in the liquid mixture, i. e. the total weight of hexane less the weight of hexane vapour. In the 5th column is given the mole fraction of hexane calculated from:

$$x_6 = \frac{1}{1 + 0.3806 \frac{g_{16}}{g_6}},$$

where the numerical factor in the denominator is the ratio of the molecular weight of hexane $M_6 = 86.17$ to that of cetane $M_{16} = 226.43$.

Column 6 and 7 contain the pressures measured as the absolute vapour pressure p when this is directly determined, or as the vapour pressure lowering, $p_0 - p$, where $p_0 = p_{6(6)} =$ the

vapour pressure of pure hexane. The figures in column 6 indicate the pressure in cm of mercury, and those in column 7 the pressure in cm of glycerine, both at a temperature of 22°. For pure hexane at t = 20°.00 we found:

$$p_{6(6)} = 131.0 \text{ cm glycerine } (22°)$$
$$= 12.145 \text{ cm Hg } (22°),$$

corresponding to the ratio 10.78_5 between the readings of the two manometers.

Finally column 8 gives the activity coefficient f'_6 calculated from (13) as:

$$f'_6 = \frac{p_6}{p_{6(6)} x_6}.$$

Heptane-Cetane. Table 4 contains the corresponding data for the heptane-cetane system at t = 20°.00, obtained from two series of independent determinations. On account of the much lower vapour pressure all the readings could be made by means of the glycerine manometer. Otherwise the methods and calculations are quite analogous to those employed in the hexane-cetane series. For pure heptane at t = 20°.00 C. we found:

$$p_{7(7)} = 39.23 \text{ cm glycerine } (22°)$$
$$= 3.55 \text{ cm Hg } (22°).$$

These figures give the ratio 10.77 between the readings of the two manometers. The slight deviation of this figure from the ratio given above is due to the use of different glycerine samples in the two cases.

The mole fraction is calculated from:

$$x_7 = \frac{1}{1 + 0.4425 \frac{g_{16}}{g_7}},$$

where the numerical factor in the denominator is the ratio of the molecular weight of heptane $M_7 = 100.20$ to that of cetane $M_{16} = 226.43$.

Table 4.

Series	g_{16}	g_V	g_7	x_7	p_7 (Gl)	log l′
1	4.2291	0.0026	0.3251	0.1480	5.24_5	$\bar{1}.9670$
		.0023	0.2868	.1329	4.71	.9668
		.0032	0.4125	.1806	6.46	.9714
		.0030	0.3871	.1714	6.10	.9687
		.0028	0.3573	.1603	5.70	.9686
		.0042	0.5860	.2384	8.59	.9743
		.0039	0.5288	.2203	7.90	.9722
		.0050	0.7268	.2797	10.15	.9774
		.0047	0.6660	.2625	9.50	.9762
		.0058	0.9096	.3270	11.96_5	.9798
		.0055	0.8277	.3066	11.18_5	.9796
		.0063	1.0238	.3536	12.94_5	.9811
		.0074	1.3139	.4125	15.24_5	.9851
		.0081	1.5339	.4504	16.70	.9867
		.0076	1.3835	.4250	15.72	.9856
		.0087	1.7610	.4848	18.01_5	.9876
		.0098	2.2628	.5473	20.48	.9907
		.0108	2.8582	.6043	22.71	.9925
		.0115	3.4444	.6480	24.43_5	.9940
		.0130	5.0183	.7284	27.61	.9963
		.0137	10.1482	.8526	32.20	.9989
		.0130	15.5072	.8923	34.08	.9995
		.0119	21.3659	$.9194_5$	35.14	.9996
		.0120	20.8186	.9174	35.03	.9994
		.0121	20.3640	.9158	34.97	$.9994_5$
		.0128	16.7936	.8997	34.36	.9995
		.0134	12.9445	.8737	33.33	.9990
		.0136	10.2380	.8455	32.24	.9989
		.0134	7.4375	.7990	30.40	.9979
		.0126	4.7833	.7187	27.23	.9960
		.0110	3.0009	.6159	23.16	.9929
		.0096	2.1366	.5332	19.90	.9897
		.0081	1.5306	.4499	16.64	.9857
		.0061	0.9811	.3440	12.57	.9805
2	5.5555	.0019	0.2882	.1049	3.71	.9658
		.0024	0.3987	.1395	4.95_5	.9679
		.0023	0.3851	.1354	4.83	.9701
		.0032	0.5574	.1848	6.62	.9716
		.0031	0.5246	.1759	6.30	.9715
		.0037	0.6533	.2099	7.54_5	.9731
		.0046	0.8678	.2609	9.45	.9764
		.0055	1.1300	.3149	11.50	.9802

Table 4 (continued).

Series	g_{16}	g_V	g_7	x_7	p_7 (Gl)	log f′
2	5.5555	0.0066	1.4846	0.3765	13.86	$\bar{1}$.9836
		.0075	1.8167	.4249	15.68	.9845
		.0083	2.1684	.4686	17.45	.9880
		.0092	2.7065	.5240	19.55	.9894
		.0097	3.1107	.5586	20.93	.9912
		.0106	3.8549	.6106	23.00	.9935
		.0113	4.6952	.6563	24.80	.9949
		.0123	6.9794	.7395	28.08	.9970
		.0111	4.5118	.6473	24.42	.9942

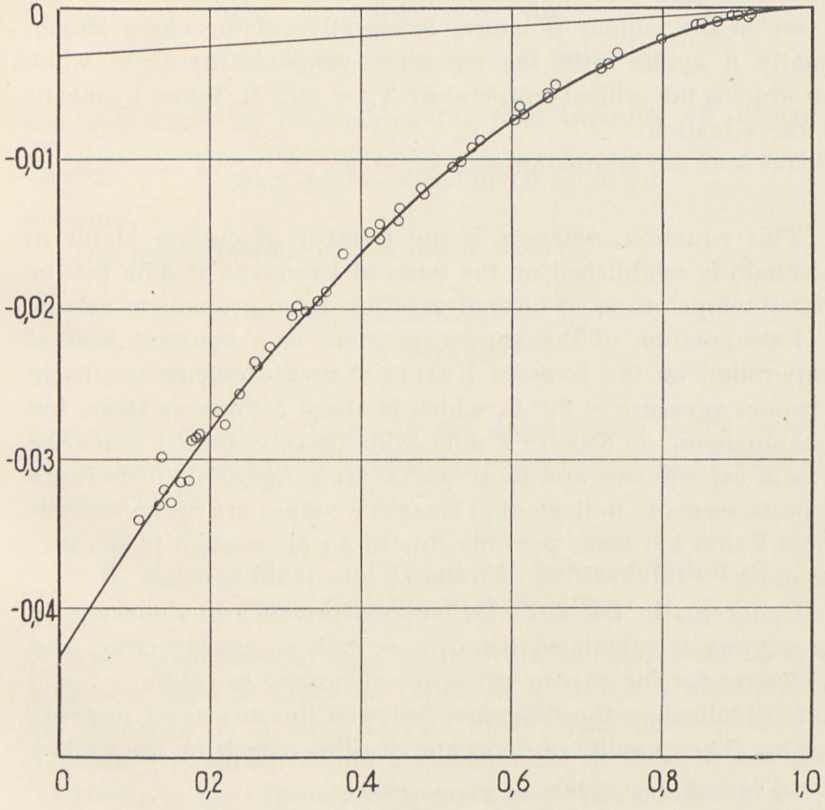

Fig. 3. Heptane-Cetane. Log f_7' against x_7.

Hexane-Dodecane. The results of similar measurements with the hexane-dodecane system are listed in Table 5. In these experiments, however, the vapour pressure of the "non-volatile" component could not be disregarded.

For the vapour pressure of dodecane we found by direct measurement at 20°.00 the value $p_{12(12)} = 0.08$ cm glycerine = 0.0075 cm Hg. This value is confirmed by the amount of dodecane carried by the hexane vapour on distillation from the flask A into the reservoirs. It is also consistent with the formula

$$p_{12(12)} = p_{6(6)} \left(\frac{p_{7(7)}}{p_{6(6)}} \right)^6 = 12.11 \cdot 0.2923^6 = 0.0076 \text{ cm Hg}$$

based upon the assumption that an increase by one in the number of carbon atoms in the chain causes the same logarithmic decrease in the vapour pressure, irrespective of the chain length. Finally it agrees with the equation, proposed by Cox[1] when introducing the critical temperature $T_c = 662°$ K. found by means of the equation:

$$\log T_c = 0.340 \log (\nu - 1) + 2.467.$$

This equation, where ν is the number of carbon atoms in the chain is established on the basis of Edmister's[2] data for the critical temperatures of normal paraffins from propane to octane.

Extrapolation of the vapour pressure at a constant heat of evaporation on the basis of Krafft's[3] measurements results in a vapour pressure at 20° C. which is about 3 times as large, but a comparison of Krafft's data with those obtained from the present experiments and those which are computable from Cox's formula seems to indicate that Krafft's values are on an average about 2 mm too high, possibly due to an air content in his preparations.

Under p_{12} in the table the vapour pressure of dodecane in the mixture is calculated from $p_{12} = 0.08\ x_{12}$ cm glycerine, and the figures for the vapour pressures of hexane in columns 7 and 8 are obtained as the difference between the measured pressure and p_{12}. The quantity of dodecane distilled over from the flask A

[1] E. R. Cox: Ind. Eng. Chem. **28**, 613 (1936).
[2] W. C. Edmister: Ind. Eng. Chem. **30**, 353 (1938).
[3] F. Krafft: Ber. d. d. chem. Ges. **15**, 1687 (1882).

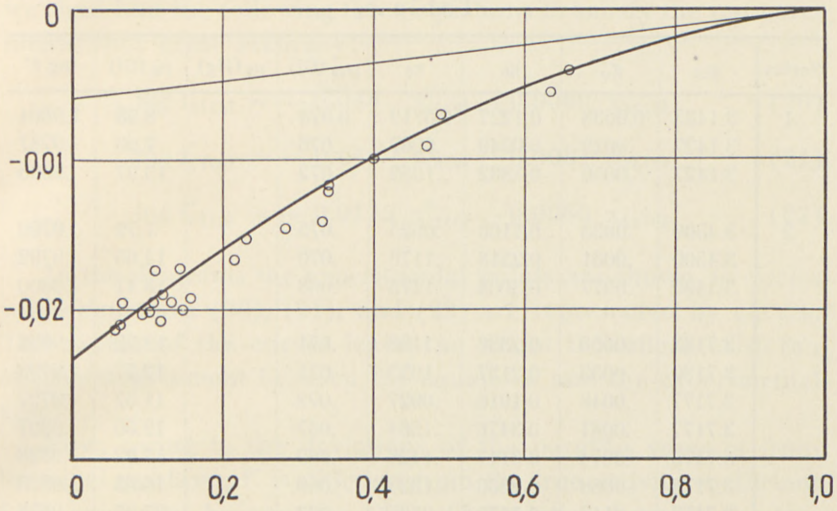

Fig. 4. Hexane-Dodecane. Log f'_6 against x_6.

was calculated by multiplying the total quantity of substance distilled over by $2 \cdot \frac{p_{12}}{p}$, where the denominator is the total vapour pressure.

The mole fraction is calculated from:

$$x_6 = \frac{1}{1 + 0.5059 \frac{g_{12}}{g_6}},$$

where the numerical factor in the denominator is the ratio of the molecular weight of hexane $M_6 = 86.17$ to that of dodecane $M_{12} = 170.33$.

8. Mathematical and Graphical Representation of the Experimental Results.

The dependence of log f′ of the volatile component upon its x-concentration as given in Tables 3, 4, and 5 is illustrated in the diagrams 2, 3, and 4. The upper right hand portion of diagram 2 is shown on an enlarged scale in the annexed plot.

Owing to the comparatively great uncertainty inherent in the method of measuring small vapour pressures, the data at x-values

Table 5.

Series	g_{12}	g_V	g_6	x_6	p_{12} (Gl)	p_6 (Hg)	p_6 (Gl)	log f'
1	3.1433	0.0038	0.1227	0.0719	0.074		8.98	$\bar{1}$.9804
	3.1427	.0029	0.0949	.0567	.076		7.06	.9787
	3.1427	.0056	0.1882	.1062	.072		13.27	.9805
2	3.4500	.0033	0.1160	.0625	.075		7.79	.9790
	3.4500	.0061	0.2318	.1176	.070		14.65	.9792
	3.4490	.0077	0.3008	.1475	.068		18.41	.9800
3	3.7182	.0058	0.2336	.1108	.071		13.92	.9826
	3.7180	.0053	0.2137	.1023	.071		12.77_5	.9798
	3.7177	.0048	0.1916	.0927	.072		11.57	.9797
	3.7177	.0081	0.3476	.1564	.067		19.56	.9807
	3.7175	.0074	0.3117	.1426	.069		17.92	.9828
	3.7173	.0069	0.2856	.1322	.069		16.53	.9805
	3.7173	.0113	0.5179	.2165	.063		27.27	.9838
	3.7173	.0147	0.7365	.2822	.057		35.71	.9859
	3.7173	.0177	0.9630	.3394	.053		43.15_5	.9879
						4.01		.9883
	3.7173	.0212	1.2537	.4008	.05	4.76		.9901
	3.7173	.0262	1.8010	.4901	.04	5.86		.9930
	3.7172	.0338	3.6451	.6605	.02	7.95		.9960
	3.7170	.0326	3.2687	.6356	.03	7.62		.9945
	3.7158	.0245	1.6573	.4694	.04	5.58		.9909
	2.7146	.0172	0.9338	.3327	.05	3.91		.9858
							42.10	.9858
	3.7135	.0120	0.5577	.2296	.061		28.98	.9848
	3.7117	.0062	0.2553	.1201	.068		15.02	.9810

below 0.06 in the case of hexane and 0.1 in the case of heptane are not sufficiently accurate and have been omitted.

Regarding the quantitative relation between f' and x it has already been mentioned in section 4 that log f' in the hexane-cetane system can be represented as a sum of two members one of which is linear, the other quadratic in x. The same is true of all the systems investigated. If for reasons to be stated below we choose the linear terms:

$$0.0060\ x_{16(6)}$$
$$0.0031\ x_{16(7)}$$
$$0.0060\ x_{12(6)},$$

we shall find the following three equations to satisfy the measurements with great accuracy:

$$\log f'_{6(16)} = -0.048 \quad x^2_{16(6)} - 0.0060 \quad x_{16(6)} \tag{20}$$

$$\log f'_{7(16)} = -0.040 \quad x^2_{16(7)} - 0.0031 \quad x_{16(7)} \tag{21}$$

$$\log f'_{6(12)} = -0.0175 \quad x^2_{12(6)} - 0.0060 \quad x_{12(6)} \tag{22}$$

In the diagrams the experimental points are shown as circles while equations (20), (21), and (22) are represented by curves. The course of the curves leaves no doubt that there exists an excellent agreement between the equations and the experimental data.

Now, owing to the deviations of the paraffin vapours from the ideal gas laws, f′ is different from the true activity coefficient f_1 as expressed by equation (15). The relation between the two coefficients can be determined from this equation by means of the known values of Δ and p_0 for the two volatile components. Introducing these values from table 1 and Section 7 we get:

$$\frac{\Delta_6}{RT} p_{6(6)} = 0.0139 = \frac{0.0060}{0.4343} \tag{23}$$

$$\frac{\Delta_7}{RT} p_{7(7)} = 0.0072 = \frac{0.0031}{0.4343} \tag{24}$$

Hence, when natural logarithms are replaced by decadic logarithms, equation (15) becomes:

$$\log f_{6(6)} = \log f'_{6(16)} + 0.0060 \quad x_{16(6)} \tag{25}$$

$$\log f_{7(16)} = \log f'_{7(16)} + 0.0031 \quad x_{16(7)} \tag{26}$$

$$\log f_{6(12)} = \log f'_{6(12)} + 0.0060 \quad x_{12(6)}, \tag{27}$$

or, inserting equations (20), (21), and (22):

$$\log f_{6(16)} = -0.048 \quad x^2_{16(6)} \tag{28}$$

$$\log f_{7(16)} = -0.040 \quad x^2_{16(7)} \tag{29}$$

$$\log f_{6(12)} = -0.0175 \quad x^2_{12(6)}. \tag{30}$$

We have thus attained the very remarkable result that the linear terms in equations (20), (21), and (22) can be accounted for as due to the effect of the deviations of the vapours from the laws of perfect gases. Removing these linear terms we arrive at expressions for the true activity coefficients f which are purely quadratic in x.

In the figures the linear member is shown by a straight line which is a tangent to the log f'-curve at $\log f' = 0$. log f is read as the vertical distance between the curve and the tangent. It is seen that the significance of the linear member is decreasing in the order: hexane-dodecane, hexane-cetane, heptane-cetane.

The data submitted convincingly show that the n-paraffin mixtures investigated are by no means ideal. On the contrary they manifest a clear deviation from the condition of ideality, as the activity coefficient of the volatile components shows a marked decrease with decreasing values of their concentration.

At infinite dilution the values calculated are:

$$\log f_{6(16)} = -0.048 \qquad f_{6(16)} = 0.895$$
$$\log f_{7(16)} = -0.040 \qquad f_{7(16)} = 0.912$$
$$\log f_{6(12)} = -0.0175 \qquad f_{6(12)} = 0.961,$$

showing in the case of hexane in pure cetane an activity coefficient more than 10 per cent. below the ideal value.

9. The Complete Curve System.

The possibility of expressing the logarithm of the activity coefficient of the volatile components in the paraffin mixtures by means of a parabolic equation is a fact of great consequence to the thermodynamics of the paraffin group on the whole. For it is known that the expression:

$$\ln f_1 = k x_2^2 \qquad (31)$$

for one component K_1 in a binary mixture by virtue of GIBBS-DUHEM's equation between the chemical potentials entails that the symmetric equation:

$$\ln f_2 = k x_1^2 \qquad (32)$$

holds for the other component K_2. It is also known that the parabolic form is the only one to permit of a complete symmetry of the curves. The ideal case follows from (31) and (32) when $k = 0$.

On account of these particularly simple conditions the following expressions result directly from expressions (28), (29), and (30):

$$-\log f_{16(6)} = 0.048 \quad x^2_{6(16)} \tag{33}$$

$$-\log f_{16(7)} = 0.040 \quad x^2_{7(16)} \tag{34}$$

$$-\log f_{12(6)} = 0.0175 \; x^2_{6(12)}. \tag{35}$$

In addition to the activity coefficients f_1 and f_2 for the two components K_1 and K_2 we shall define a composite or integral activity coefficient f_i by the equation:

$$\log f_i = x_1 \log f_1 + x_2 \log f_3. \tag{36}$$

This activity coefficient is related to the deviation of the integral work of mixing from its ideal value in the same way as f_1 and f_2 are related to the corresponding difference in the differential process of mixing. In the present case the curve representing $\log f_i$ is of course completely symmetrical with regard to the two x-concentrations, since in correspondence with (31) and (32) we have:

$$\ln f_i = k x_1 x_2. \tag{37}$$

The maximum value of $\ln f_i$ is obviously $\frac{1}{4}$ of the maximum value of $\ln f_1$ or $\ln f_2$.

In Fig. 5 $\log f_i$ is shown by the curves I, II, and III for the three systems investigated along with $\log f_{6(12)}$ and $\log f_{12(6)}$ for the hexane-dodecane system.

It cannot, however, be imagined that this simple relation should be limited to the 3 mixtures here considered. It must be assumed that it will hold good of normal paraffins generally if the number of carbon atoms in the molecules of the constituent components does not materially exceed the limits fixed by the present investigations. If we pass over to paraffins with a small number of carbon atoms, the deviation from the isochemical

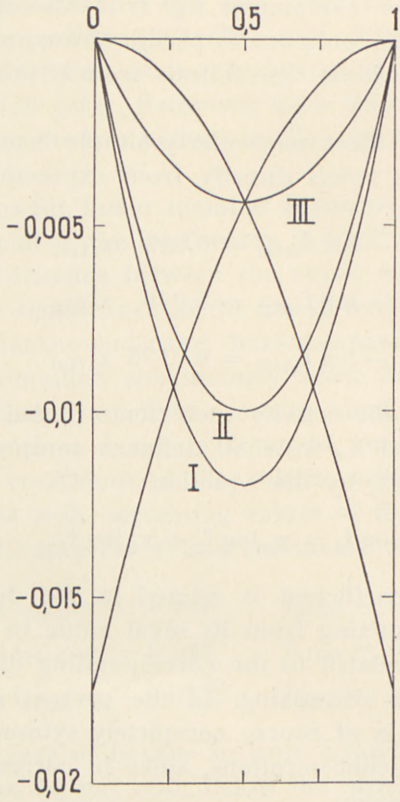

Fig. 5. Log f_i (I, II, III). Log $f_{6(12)}$ and log $f_{12(6)}$ against x.

relation will become fairly considerable, and similarly deviations are to be expected in case of very great chain length of a component.

Equations (28)—(30) and (33)—(35) may be considered special forms of the general expression:

$$\log f_{1(2)} = A \cdot x_2^2, \tag{38}$$

where A is a coefficient which at a given pressure and temperature is a function only of ν_1 and ν_2, i. e. of the number of carbon atoms in the two paraffin chains. It is a problem of special significance to determine this coefficient.

10. The Concept of Congruence. The General Equation for the Activity Coefficients of Normal Paraffins.

The concept of congruence of mixtures of normal paraffins is proposed as the basis for a general determination of their thermodynamic properties.

A mixture of the components K_1, K_2, ... containing ν_1, ν_2, ... carbon atoms per molecule, respectively, and present in the mixture in mole fractions x_1, x_2, ... may be characterized by an index ν, given by:

$$\nu = x_1\nu_1 + x_2\nu_2 + \ldots\ldots \qquad (39)$$

Mixtures with the same index are designated as congruent. They may be derived theoretically from a given mixture by transferring CH_2-groups from one paraffin molecule into another.

The theory of congruence assumes that the thermodynamic properties of a mixture of normal paraffins are determined by the index of the mixture, and that congruent solutions therefore will show the same values, e. g. for the activity coefficients of dissolved substances, irrespective of the individuality of the components.

For a pure paraffin the index is of course equal to the number of carbon atoms in the chain. In dodecane for instance we have $\nu = 12$. A mixture congruent with dodecane may be produced in an infinite number of ways. If hexane and cetane are taken as the constituent components, the composition of the mixture will be determined by the equation:

$$6x_6 + 16x_{16} = 12,$$

whence:

$$x_6 = 0.4, \quad x_{16} = 0.6.$$

The experiments which form the chief basis of the theory of congruent paraffin systems differ in nature from those submitted here, and will be dealt with in a subsequent paper. We shall here apply the theory for the purpose of determining the coefficient A in (38).

Applying (39) to a system of 2 components we have $x_1 + x_2 = 1$, and therefore:

$$x_1 = \frac{\nu - \nu_2}{\nu_1 - \nu_2}, \qquad x_2 = \frac{\nu - \nu_1}{\nu_2 - \nu_1}, \tag{40}$$

which combined with (38) gives:

$$\log f_{1(2)} = \frac{A_{1.2}}{(\nu_1 - \nu_2)^2}(\nu - \nu_1)^2 \tag{41}$$

$$\log f_{2(1)} = \frac{A_{1.2}}{(\nu_1 - \nu_2)^2}(\nu - \nu_2)^2. \tag{42}$$

By the theory of congruence f_1 depends only upon ν and ν_1. The factor:

$$\frac{A_{1.2}}{(\nu_1 - \nu_2)^2} = B$$

appearing in (41) is therefore independent of ν_2. Similarly, as f_2 depends only upon ν and ν_2, the same factor appearing in (42) is independent of ν_2. Consequently in the equation:

$$\log f_1 = B(\nu - \nu_1)^2, \tag{43}$$

where f_1 is the activity coefficient of a component K_1 in an arbitrary mixture of index ν, B is a universal constant for paraffin mixtures at constant temperature and pressure. By introduction of (40) equation (43) may be written:

$$\left.\begin{aligned} \log f_{1(2)} &= B(\nu_1 - \nu_2)^2 x_2^2 \\ \log f_{2(1)} &= B(\nu_1 - \nu_2)^2 x_1^2 \end{aligned}\right\} \tag{44}$$

and from this equation in conjunction with (28), (29), and (30) the value of the constant can be determined. The three equations in the order indicated, give the following value for B:

$$B = -\frac{0.048}{(6-16)^2} = -0.00048 \qquad \text{(hexane-cetane)}$$

$$B = -\frac{0.040}{(7-16)^2} = -0.00049 \qquad \text{(heptane-cetane)}$$

$$B = -\frac{0.0175}{(6-12)^2} = -0.00049 \qquad \text{(hexane-dodecane)}$$

These values show a very satisfactory agreement. However, as the results obtained in the hexane-cetane system are probably the more reliable of the three, we shall take $B = -0.00048$ as probably the best value. Accordingly we propose to represent the activity coefficients in normal paraffin mixtures at atmospheric pressure and $t = 20°$ C. by the expression:

$$\log f_1 = -0.00048\ (\nu - \nu_1)^2. \qquad (45)$$

Although this formula, as we are now justified in assuming, holds very closely to systems of normal paraffins from $\nu = 6$ to $\nu = 16$, it is obvious that it cannot hold by unlimited increase in the chain length. Further measurements are therefore required to test the formula outside these limits. The complete solution of the problem of the activity coefficient within the domain in which the formula is applicable naturally requires a determination of the dependence of the coefficient B on temperature. As the method used in the present work is not suited for temperatures materially above room temperature, experiments at higher temperatures based on a different principle and also including paraffins of a higher index and a correspondingly higher melting point are necessary. Such measurements are now in progress in this laboratory.

11. Summary.

1. Within certain limits of pressure and temperature paraffin vapours obey the equation:

$$p(v + \Delta) = RT,$$

where Δ is a constant.

2. An accurate method has been devised for determining the relation between composition and vapour pressure in binary mixtures in case the two partial pressures are very different.

3. Vapour pressure determinations have been made over the whole range of concentrations in the binary paraffin mixtures 6-16, 7-16, and 6-12.

4. The activity coefficient of a component K_1 in a mixture of normal paraffins containing from 6 to 16 carbon atoms is determined by the equation:

$$\log f_1 = B (\nu - \nu_1)^2,$$

where B is a constant at constant temperature, ν_1 the index of the component, i. e. the number of carbon atoms in the chain, ν the index of the mixture, defined as $\nu = \sum x_1 \nu_1$, and x the mole fraction.

5. The measurements mentioned under 3. gave the value — 0.00048 for B at 20° C.

6. Mixtures with the same ν are called congruent. On the basis of the theory of congruence the thermodynamic properties of a paraffin mixture are determined by its index ν.

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