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Addition Compounds of Urea and Organic Substances

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The inclusion of extraneous molecules in a molecular crystal usually greatly impairs its stability. Strong intermolecular forces, however, furnish a good opportunity for building into the crystal various molecules which by themselves do not appreciably contribute to the stability. Since hydrogen bonds provide relatively strong intermolecular forces, urea forms crystalline complexes with numerous substances. The complexes[1] with *n*-paraffins and their derivatives are of considerable interest for various reasons, including analytical and technical applications. The attention of this Laboratory was directed to these complexes by the work of Mr. L. C. Fetterly,[1b] who tested and greatly extended Bengen's results.[1a] The field of urea complexes with organic substances therefore has been surveyed with the object of securing a systematic description which would also furnish the basic data required for various applications.

The observation of the yield from certain specified mixtures can hardly be sufficient since it would be impossible to extend the study to a set of conditions large enough to be representative. The possible yield under any conditions can be predicted, however, at least with sufficient approximation, as soon as the standard free energy of formation is known.

In addition to the free energy, the composition of the complexes must be known for a general description of the complex formation. Data obtained for these properties are the most suitable basis for interpolations and extrapolations and for general rules regarding the influence of substituents and the structure.

The object of this work was the collection of extensive and reliable information. On the basis of the present results, improved methods for obtaining more accurate data could be developed without difficulty.

The hydrocarbon samples used were sufficiently pure to exclude any appreciable error caused by impurities. Commercial samples of the other substances were used. The influence of impurities may have slightly exceeded other errors in the case of oleic and elaidic acid.

Composition

It was soon found that separation of the complex from the mother liquor, washing and analysis leads to erratic results. Indeed, no washing agent has been found which may be relied upon to remove the adherent mother liquor without decomposing the complex to an appreciable extent. Various methods were developed which furnish reliable results.

I. **Wet Residues.**—Schreinemakers' method (analysis of the unwashed precipitate and the mother liquor) was used in two modifications. (a) In the first, one starts from a pure complex-forming substance (reactant) and an excess of unsaturated aqueous urea solution. (b) In the second modification, the complex is precipitated from an insufficient amount of powdered urea and a solution of the reactant in a non-reacting solvent.

II. **Concentration Change.**—A weighed amount of the reactant is precipitated with a weighed amount of an unsaturated aqueous urea solution. The decrease in the concentration of urea is determined. This method is by far the most convenient one. It requires some advance knowledge of the equilibrium since complete reaction can be obtained only if the final urea concentration is above the "decomposition concentration" mentioned in the discussion of the equilibrium data. Complete reaction is usually attained in one or two days. Since the decomposition concentration increases rapidly with the temperature, the maintenance of a definite temperature, 0° for complexes of low stability, is advisable.

III. **Double Concentration Change.**—For a solid such as myristic acid, one starts from a solution of the reactant in an isoparaffin and an aqueous urea solution and determines the concentration changes of both solutions.

If as in the present case extensive data are desired, the analytical methods should be simple. Non-aqueous solvents were chosen in such a manner that the refractivity was a sufficiently precise measure of the concentration. The analysis of urea solutions is conveniently and precisely carried out by evaporating a weighed sample first in a stream of air and then under reduced pressure at a temperature below 40°, and weighing the residue.

The complexes of acetone and methyl ethyl ketone were prepared in a Soxhlet apparatus under reduced pressure. The ketone, boiling at 0°, dissolved urea from the thimble. In this manner contamination of the complex formed in the distillation bulb by free urea was avoided. If the ketone and solid urea were directly mixed, it would be difficult to ensure complete reaction of the urea. The complex was then equilibrated with a ketone–toluene solution and analyzed by the method of wet residues.

1,4-Dioxane is the only reactant which was found to form two different complexes. Concordant results were obtained by method I(a) and the dew point method described in the following section. An approximate phase diagram is shown in Fig. 1.

The results are given in Table I. For *n*-paraffins the molal ratio *m*(urea/reactant) is represented (Fig. 2) by

$$m = 0.653n + 1.51 \quad (6 < n < 17) \qquad (1)$$

where n is the number of carbon atoms. This agrees with the values calculated from the results of X-ray analysis[2]

$$m = 0.6925n + 1.49 \qquad (2)$$

within the combined experimental errors of a few

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(1) (a) F. Bengen, German Patent Appl. O. Z. 12438 (1940), Technical Oil Mission, Reel 6, p. 263; (b) L. C. Fetterly, unpublished results, Shell Oil Company, Inc., Wilmington, California; (c) W. J. Zimmerschied, R. A. Dinerstein, A. W. Weitkamp and R. F. Marschner, THIS JOURNAL, **71**, 2947 (1949); paper presented at the Symposium on Adsorption, American Chemical Society, Atlantic City, September 18–23, 1949.

(2) A. E. Smith, *J. Chem. Phys.*, **18**, 150 (1950).

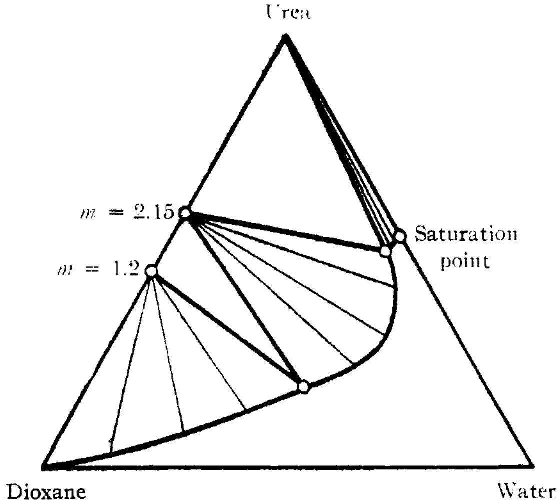

Fig. 1.—Approximate phase diagram for 1,4-dioxane at 22° (weight fractions).

per cent. The deviations of the results of Zimmerschied, *et al.*,[1c] from our data exceed our experimental errors.

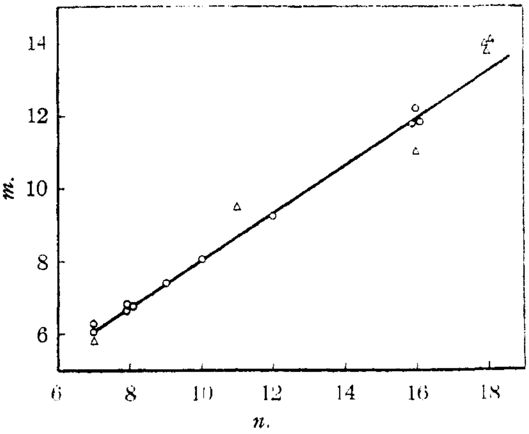

Fig. 2.—Molal ratio *m* (urea/reactant) of *n*-paraffins (*n* = number of carbons): △, Zimmerschied, *et al.*; ○, authors.

The accuracy is sufficient to exclude any possibility of representing the molal ratios by integers or quotients of small integers. A variation of the molal ratio within a finite range would be possible. The consistency of the results obtained by different methods indicates that, in agreement with the result of X-ray analysis, the width of this range is smaller than the experimental error.

Equilibrium

The change of free energy will be represented by the equilibrium constant *K* of the decomposition reaction

$$\text{complex} = \text{reactant} + m \text{ urea}$$

According to this definition the value of *K* is equal to the mole fraction of the reactant in a perfect solution which is in equilibrium with the complex and solid urea. This is convenient in recovery problems. The reciprocal of *K* is a measure of the stability of the complex.

Table I

Composition of Urea Complexes and Increase of Heat Content on Decomposition

Reactant	Molal ratio urea/reactant	Weight ratio urea/reactant	ΔH, kcal./mole
Acetone	3.39	3.5	..
Methyl ethyl ketone	3.78	3.15	4.7
Adipic acid	5.3	2.2	3.3
n-Heptane	6.1	3.7	7.3
n-Octane	6.73	3.54	9.7
Octene-1	6.3	3.4	7.3
trans-Octene 2	6.6	3.5	6.6
cis-Octene-2	6.5	3.5	..
Octanol-1	6.7	3.1	7.3
Octanol-2	6.4	3.0	6.6
Di-*n*-butyl ether	6.5	3.0	9.3
Caprylic acid	6.6	2.7	10.0
n-Nonane	7.4	3.47	11.8
n-Decane	8.1	3.4	13.1
Decene-1	7.8	3.3	11.6
1-Bromodecane	8.9	2.4	14.7
2-Bromodecane	7.6	2.1	..
Undecene-1	8.8	3.4	14.4
Undecylenic acid	7.9	2.6	19.7
Methyl undecylenate	9.5	3.0	17.0
Dodecane	9.3	3.3	16.1
Dodecene-1	9.3	3.3	12.6
Lauryl alcohol	9.5	3.1	15.6
Lauryl chloride	10.6	2.9	16.3
Lauryl bromide	10.4	2.5	15.2
Myristic acid	11.1	2.9	22.5
Hexadecane	11.95	3.2	21.0
Hexadecene-1	12.0	3.2	23.5
Oleic acid	12.2	2.6	27.4
Methyl stearate	14.8	3.0	19.0
Methyl oleate	14.5	2.9	25.0
Methyl linoleate	14.2	2.9	24.6
Methyl linolenate	13.7	2.8	22.5
1,4-Dioxane	1.2	0.82	2.4
1,4-Dioxane	2.15	1.5	5.7

For determining or using the equilibrium constant

$$K = a_r a_u{}^m \tag{3}$$

we have to know the activity a_r of the reactant and the activity a_u of urea. Sufficient information is available for activity coefficients in mixtures of *n*-paraffins and other hydrocarbons of moderate molecular weight. The activities of urea in aqueous solution, referred to solid urea as reference state, have been calculated by Dr. J. N. S. Kwong from available data.[3] The results are given in Fig. 3. The accuracy of the data for 0 and 25° is much higher than

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[3] (a) G. Scatchard, W. J. Hamer and S. E. Wood, This Journal, **60**, 3061 (1938); (b) F. T. Gucker, Jr., and H. B. Pickard, *ibid.*, **62**, 1464 (1940); (c) A. N. Krasilchikov and S. S. Trainina, *J. Phys. Chem.*, *USSR*, **13**, 281 (1939).

required. The data for 40 and 70° are sufficiently accurate for the present purpose.

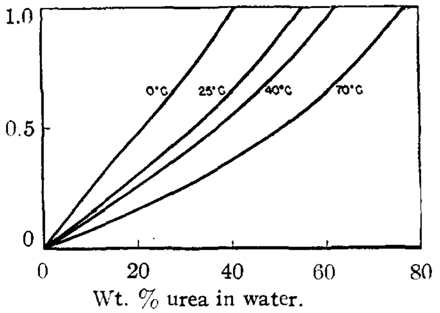

Fig. 3.—Activity a_u of urea in aqueous solution (a_u = 1 for solid urea).

In the determinations of K only hydrocarbon mixtures and aqueous solutions were used. The presence of a ketone or alcohol would have offered the considerable advantage of a quicker approach to equilibrium but the disadvantages of more complicated analyses and lack of data for activities would have been serious. Various methods have been developed.

I. **Aqueous Reaction.**—Equilibrium is established between the pure reactant, an aqueous urea solution and the complex. The concentration of urea is determined. Since $a_r = 1$, K is given by the urea activity and the molal ratio m. Since the urea concentration can be easily determined within a few hundredths of one per cent., the sensitivity of the result to analytical errors is no serious disadvantage.

II. **Non-aqueous Reaction.**—Equilibrium is established between a solution of the reactant in a non-reacting hydrocarbon and powdered urea. The concentration is determined. The activity coefficients must be known. This method is convenient and relatively precise if a solvent of suitable refractivity is chosen. The approach to equilibrium is slow.

In both methods approach to equilibrium must be carefully checked. Addition of solvent or reactant and temporary temperature changes are useful in ascertaining equilibrium. The long duration (several days or weeks) of each test is only a minor disadvantage since an observer can handle a considerable number of tests at the same time.

III. **Dew Point.**—This method is based on the relation

$$K = p/p^0 \qquad (4)$$

where p^0 is the vapor pressure of the reactant and p the decomposition pressure, *i. e.*, its partial pressure in the presence of complex and solid urea. A static determination of p would be inconvenient because of the difficulty of removing gaseous impurities; a dynamic method cannot be used because equilibrium cannot be attained. The determination of p by means of the corresponding dew-point furnishes good results if p amounts to at least a few mm. The apparatus is shown in Fig. 4. A sample of the complex is placed in the bottom of the vessel and stirred by a small bar-magnet which is turned by a motor-driven magnet below the bath. The dew surface is arranged behind a flat window in the vessel. The temperature of the dew surface is controlled by pumping water from a variable temperature bath over the inside of the dew surface. The water circulation tube is enclosed in a vacuum jacket so that the dew surface is the only cool spot in the vapor space. A baffle protects the dew surface from contamination with the solid.

Since organic substances condense in a film, a shiny mirror is entirely unsatisfactory as dew surface. A dull ground glass surface (3F carborundum powder) is nearly opaque when dry and becomes transparent on condensation of an organic substance. The difference between dew point readings on cooling and heating usually was 0.1° for a pure liquid, 0.5° for a complex.

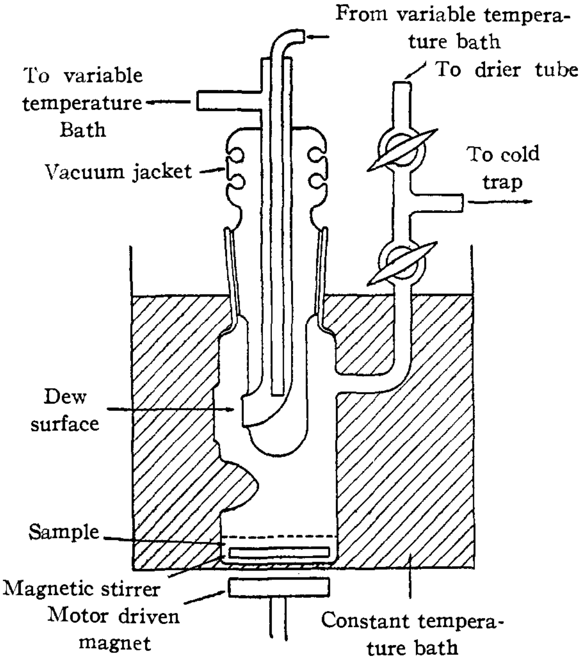

Fig. 4.—Dew point apparatus.

If the bath temperature exceeds 40° the dew surface is kept at a lower temperature only during the actual readings so that sublimation of urea is avoided.

The apparatus can be used for the determination of both m and K. A sample of the complex containing excess reactant is introduced. The vessel is repeatedly evacuated for a short time by connection with a buffer flask until the dew point falls below that of the pure reactant. All reactant withdrawn after this time is collected in a cold trap. Approach to equilibrium between vapor and solids is observed by means of several dew point readings during

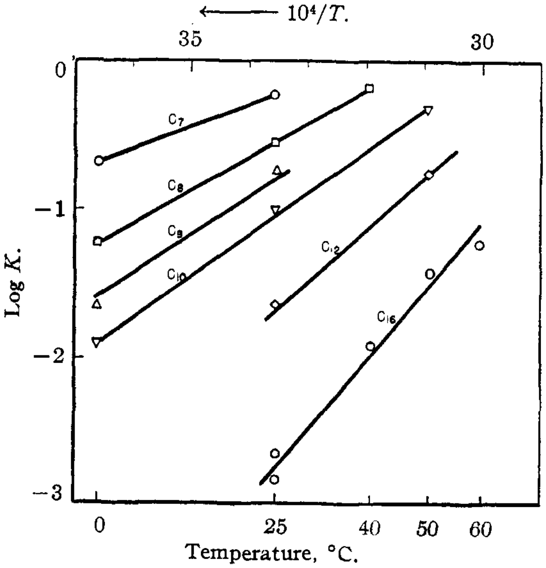

Fig. 5.—Equilibrium constants (*n*-paraffins).

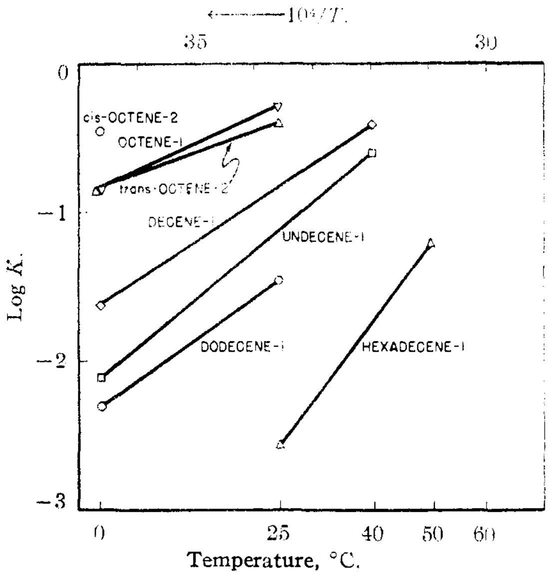

Fig. 6.—Equilibrium constants (*n*-olefins).

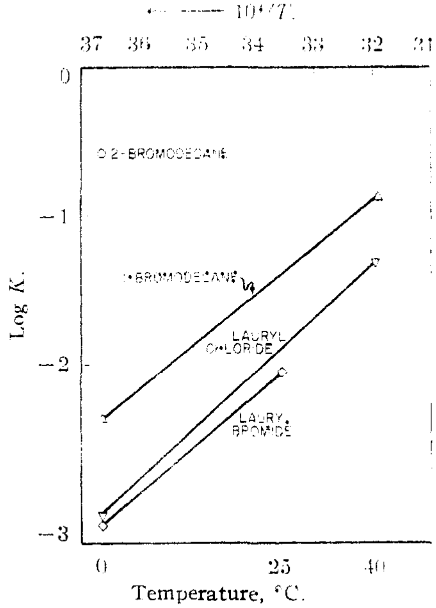

Fig. 7.—Equilibrium constants (halides).

a few hours. Evacuation and dew-point readings are repeated once or twice. Then the complex is decomposed by full evacuation and, if necessary, heating. The content of the cold trap and the residual urea are weighed. This method has been used to check the composition of the two dioxane complexes and to determine their equilibrium constants. In general, the separate determination of *m* is preferable. In this case the cold trap is discarded and a sample containing excess urea is introduced.

The results of the three methods were checked against each other. Obviously their use may be extended to the investigation of other molecular compounds.

Discussion of the Equilibrium Data

The logarithms of the equilibrium constants *K* of the decomposition reaction are shown in Figs. 5–10 as functions of $10^4/T$. The increase of heat

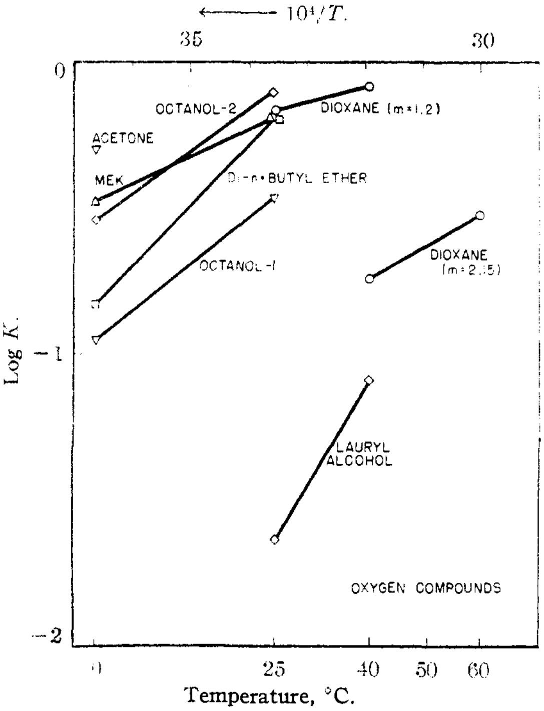

Fig. 8.—Equilibrium constants (oxygen compounds).

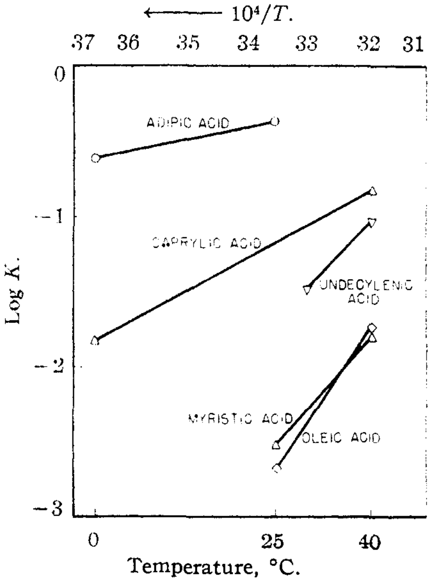

Fig. 9.—Equilibrium constants (acids).

content on decomposition (or the heat of formation) in kcal./mole reactant, calculated from the slopes of log *K*, is given in Table I. The error may exceed 1 kcal./mole in a few cases.

The values of *K* for any *n*-paraffin up to cetane can be read off Fig. 11. The heats of formation are given in Fig. 12. The agreement with the values of Zimmerschied, *et al.*,[1c] is good.

The heats of formation (Table I) may be crudely interpreted as due mainly to the heat of

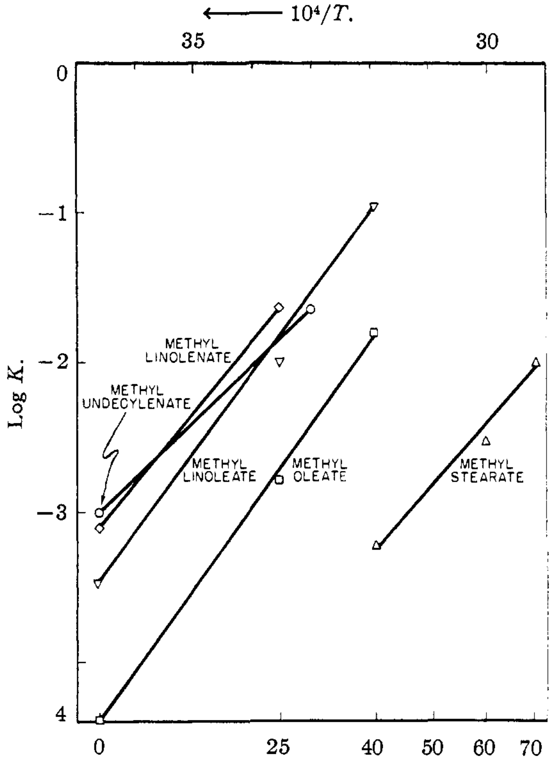

Fig. 10.—Equilibrium constants (esters).

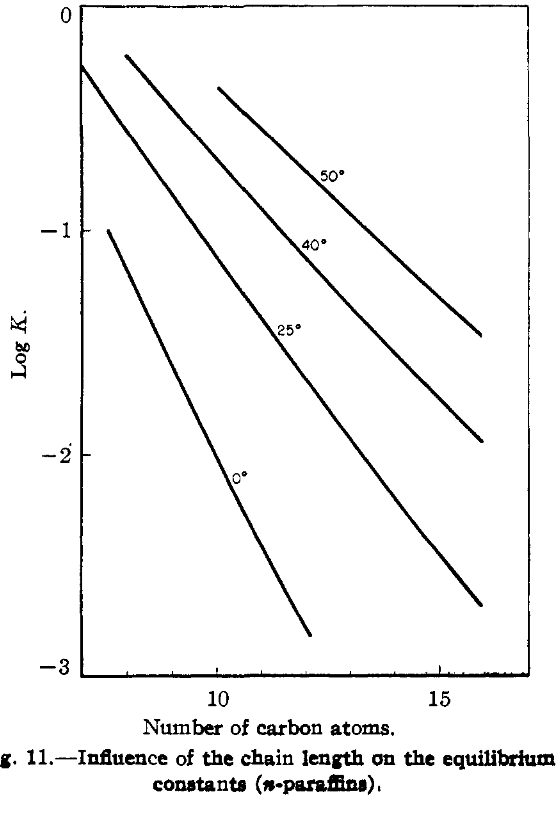

Fig. 11.—Influence of the chain length on the equilibrium constants (*n*-paraffins).

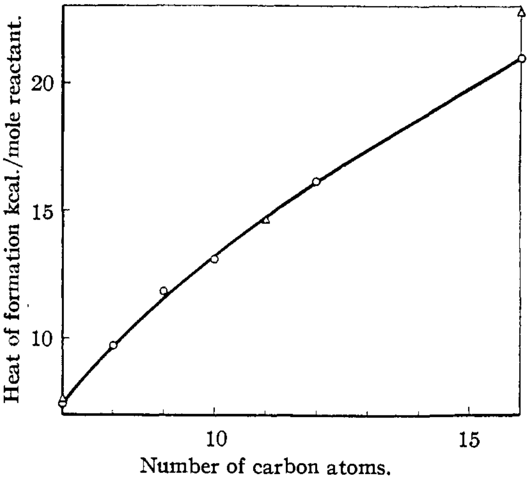

Fig. 12.—Heat of formation (*n*-paraffins): △, Zimmerschied, *et al.*; ○, authors.

fusion and the difference in the energy of the hydrogen bonds between the urea in the complex and pure urea.

With a few characteristic exceptions, linear relations hold in a roughly approximate way between log K (25°), the heat of formation (increase in heat content on decomposition) ΔH and the molal ratio m (Figs. 13–16). The straight lines in these figures represent the equations

$$\log K = 2.20 - 0.403m \quad (25°) \qquad (5)$$

$$\Delta H = -6.5 + 2.37m \quad (\text{kcal./mole}) \qquad (6)$$

The exceptions are dioxane, the ketones, acids and esters. The deviations may be partly due to differences in the heat of fusion but also to specific interaction of functional groups with the urea. These relations are useful for supplementing the available data.

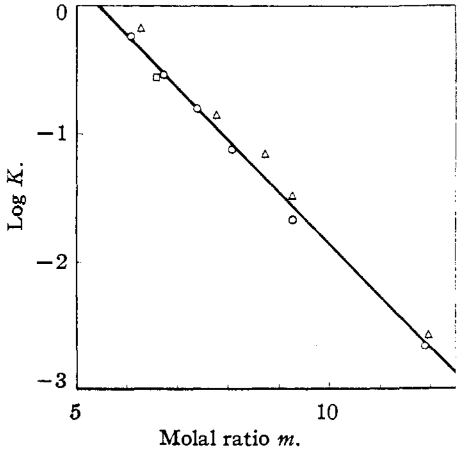

Fig. 13.—Equilibrium constant at 25° and composition (hydrocarbons): ○, *n*-paraffins; △, 1-olefins; □, *trans*-octene-2.

For the interpolation, extrapolation and estimation of K a diagram of K/K_P against n is useful.

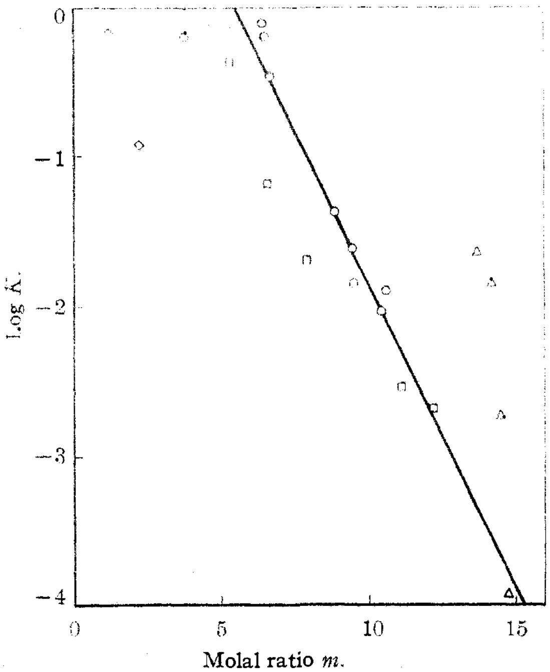

Fig. 14.—Equilibrium constant at 25° and composition (non-hydrocarbons): ◇, dioxane; □, acids; △, C_{18} methyl esters; ○, other compounds. The straight lines in Figures 13 and 14 represent eqn. (5).

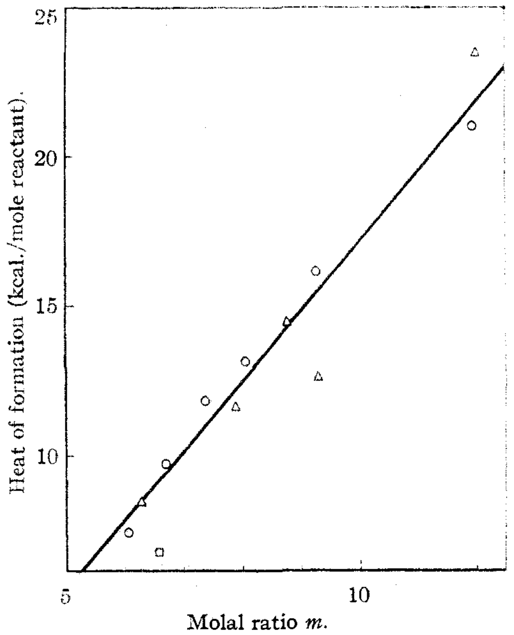

Fig. 15.—Heat of formation and composition (hydrocarbons): ○, n-paraffins; △, 1-olefins; □, *trans*-octene-2.

In this diagram n is the number of carbon atoms, K the equilibrium constant of the members of a homologous series and K_P that of the corresponding n-paraffins. The values for K/K_P approach unity with increasing n.

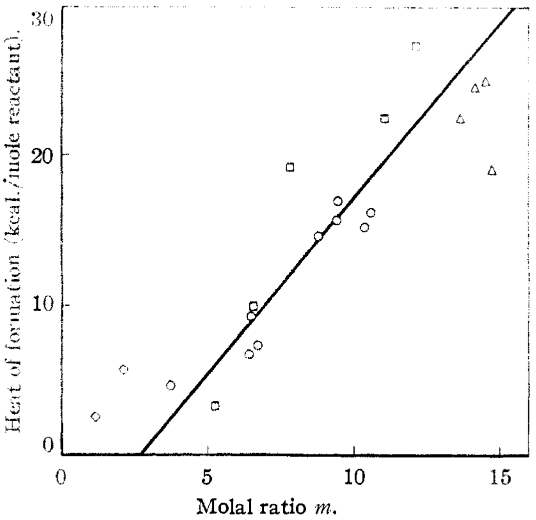

Fig. 16.—Heat of formation and composition (non-hydrocarbons): ◇, dioxane; □, acids; △, C_{18} methyl esters; ○, other compounds. The straight lines in Figures 15 and 16 represent eqn. (6).

The knowledge of K and m together with sufficient information regarding activity coefficients permits the prediction of the maximum yield and various other basic data for applications in which a single substance is precipitated. The diagrams in Figs. 17 and 18 illustrate a few details. The equilibrium between a n-paraffin in a hydrocarbon mixture and an aqueous urea solution is described by Fig. 17. The rapid increase of the mole fraction of the paraffin with decreasing urea concentration emphasizes the importance of maintaining urea saturation. The stability field of a n-paraffin complex is described by Fig. 18. The top line (saturation curve)

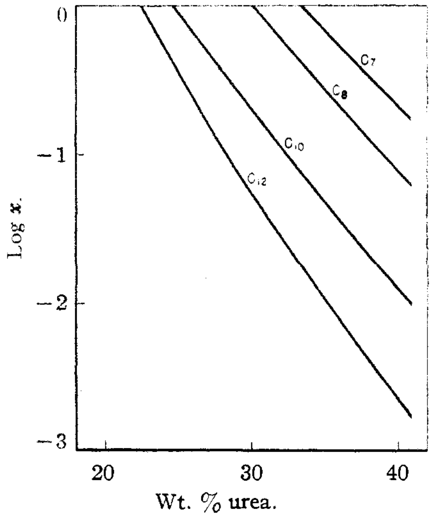

Fig. 17.—Influence of urea concentration on the equilibrium mole fraction x of n paraffins (aqueous urea solutions at 0°).

indicates the solubility of urea in water. A complex is stable in contact with an aqueous solution if the urea concentration exceeds a certain value, the "decomposition concentration." The decomposition line indicates the decomposition concentration for any temperature. The stability field is enclosed by the saturation line and the decomposition line. These two curves intersect at the decomposition temperature, for which $K = 1$. Above this temperature the pure complex does not exist under any conditions.

Mixtures of Reacting Substances

Applications usually involve mixtures containing several complex-forming substances. Two different cases may be taken into consideration: (a) each complex represents a separate solid phase. (b) A single solid phase, *i. e.*, a solid solution of all reacting substances in urea, exists. According to the results of crystal structure analysis[2] case (b) rather than (a) is to be expected.

The two cases can be distinguished by an examination of a mixture of two *n*-paraffins and another hydrocarbon (*n*-heptane, *n*-octane, decalin at 0°) and solid urea. In case (a) the mole fractions x_7 and x_8 in the mother liquor cannot fall below the values K_7 and K_8 of the respective equilibrium constants. Actually it has been found that they approach much lower values, which satisfy the relation

$$x_7/K_7 + x_8/K_8 = 1 \qquad (7)$$

The precipitate therefore is a single solid solution. The complex formation can be completely described under the plausible assumption that the activity of any reactant in the solid solution is equal to its mole fraction y_j calculated on a urea-free basis (y_j = number of moles of j divided by the total number of moles of reactants in the solid). The equilibrium constants obtained in the preceding section, therefore, are represented for mixtures by

$$K_j = a_j a_u^{m_j}/y_j \qquad (8)$$

where a_j indicates the activity of j in the mother liquor and m_j its molal ratio. Eqn. (7) follows from (8) for the special case tested since $y_7 + y_8 = 1$.

It is immediately seen that the ratio of two equilibrium constants

$$K_1/K_2 = (a_1y_2/a_2y_1)a_u^{m_1-m_2} \qquad (9)$$

plays the same role in urea separation as the relative volatility in distillation if

$$m_1 = m_2 \qquad (10)$$

or if solid urea is present. Equation (9) is useful for a direct determination of the ratio of two equilibrium constants.

Most questions regarding the precipitation from reactant mixtures can be reduced to the following problem: given the mole fractions z_i of the reactants and the mole fraction $1 - z$ of all non-reacting components where

$$z = \Sigma z_i \qquad (11)$$

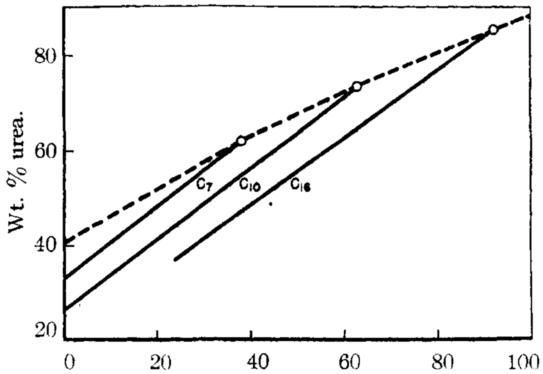

Fig. 18.—Stability fields of *n*-paraffins (O, decomposition points; broken line, saturation curve; solid lines, decomposition curves).

The equilibrium constants K_i are known. The mole fractions x_i in the mother liquor and y_i in the precipitate after treatment with an excess of solid urea are to be found. The calculation will be simplified by the assumption that all activity coefficients are unity (if not, the quantities K_i in the following derivation are to be replaced by K_i/γ_i). The equilibrium condition is

$$K_i = x_i/y_i \qquad (12)$$

With

$$x = \Sigma x_i \qquad (13)$$

the material balance for a mixture containing 1 mole of non-reacting solvent is represented by

$$z_i/(1 - z) = x_i/(1 - x) + y_i(z - x)/(1 - z)(1 - x) \qquad (14)$$

Elimination of y_i from (12) and (14) furnishes

$$x_i = z_iK_i/z[1 + (1 - z)(K_i - x)/z(1 - x)] \qquad (15)$$

where x is determined by the condition

$$\Sigma y_i = \Sigma x_i/K_i = 1 \qquad (16)$$

Eqns. (15) and (16) can be solved by approximation. Abbreviating

$$\bar{x} = \Sigma z_iK_i/z \qquad (17)$$

we obtain the second approximation

$$x_i = (z_iK_i/z)[1 - (1 - z)(K_i - \bar{x})/z(1 - \bar{x})] \qquad (18)$$

This approximation, which satisfies (16), is in general satisfactory. The first approximation, obtained by omitting the term in brackets, is frequently insufficient.

Several tests with mixtures of heptane and octane, octane and decane, octane and methyl ethyl ketone were found to be in satisfactory agreement with (18).

An inspection of (18) shows that as a first approximation a reactant's contribution to the mother liquor is proportional to both its original mole fraction and its equilibrium constant. Practically, the effect is the same as if the original mixture had been split before addition of urea into parts containing only one reactant. The term in brackets, however, increases the equilibrium concentration of the most stable reactant ($K_i < \bar{x}$) and decreases that of the least stable reactant ($K_i > \bar{x}$).

From a mixture even a substance whose complex is unstable by itself ($K_i > 1$) can be precipitated. Conversely, a value $K_i > 1$ can be determined by investigation of a mixture with the aid of eqn. (9). From observations made on a mixture of *n*-heptane and 2-methylnonane it was found that the equilibrium constant of the latter lies between 3.1 and 4.4 (25°). In a similar way the upper limit 3.2 (25°) was obtained for 7-methyltridecane. Comparing these values with those of the corresponding *n*-paraffins one sees that appreciable contamination of a *n*-paraffin below C_{16} with 2-methyl paraffins but hardly with other isomers is to be expected. The addition products of longer chains may also contain other isomers.

A variety of other problems can be solved by means of the relations derived in this section. For instance, the separation efficiency under equilibrium conditions can be represented as a function of the recovery.

The use of equilibrium constants for describing molecular complexes and the methods presented for determining equilibrium constants obviously can be extended to other complexes. The relations derived for mixtures of reacting substances are restricted by the conditions that a single solid phase is formed and that the activity of a reactant is equal to its number of moles in the solid divided by the total number of moles of reactants in the solid. These conditions may be expected to be satisfied in many cases.

The recent paper of Schlenk[4] partially overlaps with the work reported here. Schlenk's results for the composition of the complexes, with the exception of that of acetone, are in excellent agreement with ours. In the case of acetone we had anticipated difficulties because of the solubility of urea in acetone, the miscibility of acetone with urea solvents and the resulting danger of salting-out effect. For these reasons we devised the Soxhlet method described before.

Schlenk's heats of formation are far below our results and in general below those of Zimmerschied, *et al.*[2c] The reason is undoubtedly incomplete reaction in his calorimetric determinations. We had previously observed that the reaction with solid urea in absence of a solvent proceeds quite rapidly to a certain extent, apparently until the urea grains are covered with the complex. Later the rate is extremely low although the reaction is still far from complete.

Two results of Schlenk furnish directly equilibrium constants. His dissociation pressures for heptane are in fair agreement with our equilibrium constants, those for octane far too low. He found that the ratio of 3-methylheptane to *n*-hexane or *n*-octane in the complex is the same as in the original liquid. This result is entirely inconsistent with the equilibrium conditions which we derived for mixtures.

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Summary

1. Methods for determining the composition of solid urea complexes and for measuring the equilibrium constant of the decomposition have been developed. These methods can be applied to the examination of other molecular compounds of high or low stability.

2. Data are presented for the urea complexes of *n*-paraffins, *n*-olefins, halides, alcohols, ketones, acids and methyl esters, an ether and dioxane. Two addition compounds of dioxane have been found. The composition of all other complexes is given by a single definite value.

3. The heats of formation have been obtained from the temperature dependence of the equilibrium constant. Linear relations between the molal ratio (urea/reactant), the free energy and the heat of formation hold approximately for most of the complexes.

4. The data furnish a complete description of the *n*-paraffin complexes between C_7 and C_{16}. Data for a large field of derivatives can be estimated by systematic comparison of the results presented.

5. A mixed complex (single solid phase) is formed from a mixture of reactants. A complete and sufficiently accurate description of the equilibrium of mixtures can be derived from the data obtained for pure complexes.

6. A substance which by itself does not form a stable complex can be precipitated from a mixture. This is to be taken into consideration in practical applications. Crude values of the equilibrium constants of the unstable complexes of 2-methylnonane and 7-methyltridecane have been obtained.

7. The composition and equilibrium constants of the complexes together with the activity coefficients of the mother liquor are sufficient for the prediction of efficiency, yield, recovery, etc., under equilibrium conditions for the process of complex formation. Application of the results is illustrated by a diagram for the influence of the aqueous urea concentration on the equilibrium and by a diagram of stability fields.

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[4] W. Schlenk, Jr., *Ann.*, **565**, 204 (1949).