NOTE.

The Iodine Coulometer and the Value of the Faraday. A Correction.—Professor G. P. Baxter has kindly called our attention to the fact that 0.0099% should have been added to, instead of subtracted from, the apparent weight of iodine in applying the vacuum correction.[1] When this error is corrected the electrochemical equivalent of iodine becomes 1.31491 mg. per coulomb and the faraday (assuming I = 126.92) 96,524 coulombs per equivalent. This result agrees within 0.03% with the value 96.494 (Ag = 107.88) calculated from the electrochemical equivalent of silver (1.11804) obtained by Rosa, Vinal and McDaniel. If, instead of using the International Atomic Weights for 1912, as above, we employ the ratio of silver to iodine as directly determined by Baxter[2] our results then give 1.11755 milligrams as the electrochemical equivalent of silver, as against the value 1.11804 obtained by Rosa, Vinal and McDaniel. The difference is partly accounted for by the presence of moisture and other included material (0.01 to 0.02%) in their silver deposit and partly by the difficulty of reproducing exactly the experimental conditions of Smith, Mather and Lowry upon which our preliminary determination was based.

An extensive series of comparisons between the iodine coulometer and the silver coulometer of the type employed at the Bureau of Standards will be undertaken shortly and should lead to a determination of the value of the faraday with a certainty of 0.005%. S. J. BATES.

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THE FREE ENERGY OF ORGANIC COMPOUNDS. I. THE REVERSIBLE SYNTHESIS OF UREA AND OF AMMONIUM CYANATE.

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As an introduction to this series of investigations upon equilibrium in organic reactions, we may consider briefly the nature of the problems which are capable of solution by aid of free energy measurements. Since organic chemistry is characterized by the enormous number of compounds derived from a few elements, there are in a given system not merely one or two, but usually a very large number of reactions which are stoichiometrically possible and involve only known substances. Under a given set of conditions some of these will be found to occur, others will not. But this distinction furnishes no adequate basis for a rational classification. Whether a given reaction does or does not occur to an observable extent depends often upon the length of time during which observations are made.

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[1] THIS JOURNAL, 34, 1366

[2] *Ibid.*, 32, 1602.

To every conceivable chemical reaction can be ascribed a tendency, under given conditions, to run in one direction or the other. The factors which determin the velocity of such a reaction, although of great inherent interest, are not the ones with which we are at present concerned. Indeed, before these factors can be satisfactorily investigated we must distinguish sharply between the reactions which, in the absence of suitable catalyzers, do not proceed with measurable velocity, and those reactions which are thermodynamically impossible.

A reaction is thermodynamically possible when, and only when, under the given conditions, the total free energy of the products is less than that of the substances entering into the reaction. It is only when the difference of free energy between the factors and the products is zero that true chemical equilibrium exists.

A mixture of oxygen, hydrogen and water vapor at ordinary temperatures undergoes no observable change. But a reaction is thermodynamically possible and can in fact be made to take place in the presence of platinum sponge. By diminishing very greatly the concentrations of oxygen and hydrogen, it would be possible to reach a point where the free energy of these gases would equal that of the water vapor. Then the reaction would occur in neither direction, no matter what catalyzer might be added. At even lower concentrations of the elements the reverse reaction, the dissociation of water, would be the one thermodynamically possible. We have emphasized this distinction between the tendency to react and the rate of reaction because of the not infrequent confusion of ideas exhibited by the erroneous assumption that chemical affinity is measured by reaction velocity. Thus, when a certain system is said to be stable, it is often meant that no rapid reaction occurs.

The study of free energy affords the only true measure of chemical affinity, and although, when the free energies of all the substances involved in a given reaction are known, it may still be impossible to predict the rate of the reaction, it will be possible to state in advance in what direction and to what extent the process can ultimately occur. This will be an advance of no small importance.

The field of organic chemistry is especially rich in the so called "reversible reactions," that is, reactions in which equilibrium exists under such conditions that all the reacting substances are present in measurable amounts. Whenever such an equilibrium is found it is possible to study the change of free energy which accompanies the reaction. In a systematic tabulation of free energies it is, however, of the greatest convenience to know the free energy of a large number of important compounds referred directly to the elements of which they are composed. In other words, we desire the free energy change accompanying the formation of each substance from its elements.

In order to obtain thus the free energy of an organic substance, it is necessary to synthesize it from its elements by a series of processes in each of which a true equilibrium is investigated. Such a procedure we shall term a reversible synthesis.

If such a reversible synthesis can be carried out for a few typical compounds, then through a study of already known equilibria involving these substances, a very large number of free energy values can be readily obtained.

In a preliminary investigation we have found a number of reactions, a study of which seems likely to afford several important reversible syntheses. Of these the most promising was the synthesis of urea and ammonium cyanate from ammonia, carbon dioxide and water, for each of which three substances the free energy has already been determined. From the cyanate it will then be no difficult task to determin the free energy of hydrocyanic acid. This is, for our purpose, one of the most important of substances, since it enters into a very large number of reactions of various types.

The experiments and the somewhat complicated calculations, which in the present investigation have led to the desired results, will be treated in some detail, not merely because they have furnished the most direct method of attacking this special problem, but also because they illustrate the nature of the difficulties which are likely to be met in this kind of an investigation, and some typical ways in which such difficulties may be overcome.

The Equilibrium between Urea, Carbon Dioxide, Ammonia and Water.

At room temperature the hydrolysis of urea in aqueous solution proceeds at an inappreciable rate. At temperatures above 140°, on the other hand, there is danger of complicating side reactions. The temperatures chosen for the following experiments were 132°, 111° and 77°, the boiling temperatures of commercial amyl alcohol, toluene, and carbon tetrachloride.[1] Sealed glass tubes containing aqueous solutions of urea after heating until equilibrium was presumably established, were cooled rapidly and their contents analyzed. The solution always contains ammonium carbonate and carbamate (together with their products of hydrolytic and electrolytic decomposition), ammonium cyanate and urea. In our experiments, the cyanate never amounted to more than 0.1% of the total salt and may, therefore, for the moment, be neglected. It was planned to determin the carbonate and carbamate together by precipitation as barium or calcium carbonate and to obtain the urea by

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[1] The vapor baths used in this investigation were heated electrically by a coil placed directly in the boiling liquid. They proved very satisfactory and could be used continuously for many days without a change of temperature of more than 0.5°

difference.[1] The percentage of urea, however, left in equilibrium proved in all cases to be so small that it was necessary, for the sake of accuracy, to determin it directly. This was first attempted by evaporating off the water and ammonium salts and weighing the residue as urea. It was found, however, that the glass containing tubes were attacked by the solution during the prolonged heating necessary for the establishment of equilibrium and this caused a considerable increase in the weight of the residue. The use of Jena glass tubes did not altogether obviate this difficulty. Therefore, since the foreign substances mixed with the urea proved to be insoluble in alcohol, the residue was leached with absolute alcohol and the resulting solution of urea carefully evaporated *in vacuo* in a shallow horizontal tube; this left pure urea, which, as before, was weighed. The temperature during the evaporation was not allowed to exceed 40°, as it was feared that at higher temperatures the urea might be converted in part into volatil ammonium cyanate.

In order to test the adequacy of this method of analysis, several mixtures of ammonium carbonate with known amounts of urea were evaporated and the residues weighed. In all these experiments there was a slight, but negligible, loss of urea. Thus, in one experiment the residue was twice redissolved and evaporated. The original weight of the urea was 0.4232 gram, which, after the successive evaporations, became 0.4222, 0.4216 and 0.4213 gram. This method, therefore, is accurate at least within 0.5%, which suffices for our purpose. In many of the later experiments, however, this method was replaced by another which is at the same time more accurate and more convenient and which consisted in subjecting the urea residue to a simplified form of the Kjeldahl determination for nitrogen. Whenever both methods were simultaneously employed, identical results were obtained.

The first experiments were made with molal solutions of urea at 132°, but it soon became evident that the hydrolysis of the urea was so nearly complete as to render accurate analysis impossible. With solutions of higher concentration a larger percentage of urea in the equilibrium mixture was to be expected and in the next experiments a solution con-

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[1] It is interesting to note that a solution containing urea, together with ammonium carbonate, carbamate and cyanate, can be completely analyzed by a single precipitant. If the solution is cooled to 0° and an excess of barium hydroxide be added, the carbonate precipitates as barium carbonate and may be filtered before any precipitate is formed from the carbamate. The filtrate then, on warming or longer standing, yields a further precipitate of barium carbonate equivalent in amount to the carbamate present. If the solution is once more filtered and the new filtrate acidified and then made alkalin again, the cyanate is precipitated as barium carbonate. Finally, after this precipitate is removed, if the solution is boiled the urea will be gradually hydrolyzed and precipitated as barium carbonate. Owing to the great differences in the amounts of the substances present in our solutions this method was not available.

taining 10 mols of urea per liter was used. The following results were obtained in these experiments:

TABLE I.

Experiment.	Duration of heating (hrs.).	Weight solution. Grams.	Initial urea content. Grams.	Wt. urea in residue. Gram.	Per cent urea left.
[1	24	2.132	1.116	0.0958	8.6]
2	48	1.952	1.021	0.0950	9.3
3	200	2.114	1.106	0.1162	10.5

The analysis in the first experiment was not entirely satisfactory and a small amount of urea may have been lost. The results show that equilibrium was doubtless established in all three cases, in fact the amount of urea left was greatest in the solution which was heated for the longest time. The cause of the small difference between the results of the last two experiments was not further investigated, since it was decided to continue the experiments with a somewhat less concentrated solution, owing to the fact that the strong solution produced too much carbonate to remain dissolved when the tubes were cooled.

In all the preceding experiments, care had been taken to provide that the tubes should be completely full of solution (within a few hundredths of a cc.) at the temperature of the heating bath. This precaution was necessary, since at the high temperature the pressure of carbon dioxide and ammonia is so great that a considerable portion of the ammonium carbonate would otherwise have been in the gaseous space. Apparently, however, a diminution in volume accompanied the hydrolysis of urea, so that the tubes, even though completely filled at the outset, showed a considerable vapor space at the end of the heating. For this reason, we decided to start with a solution of ammonium carbonate or carbamate instead of urea. Ammonium carbamate was prepared by passing carefully dried carbon dioxide and gaseous ammonia into absolute alcohol, as described by Mente,[1] and washing the solid product with ether. The product was dried for a few minutes in an air bath at 100°.

Equilibrium Measurements at 132°, 111° and 77°.—A solution containing 1 gram of this carbamate to 1.5 grams of water was used in the following equilibrium experiments, which will be known as Solution A. The result of heating four samples of this solution at 312° is shown in the following table:

TABLE II.

Experiment.	Hrs. of heating.	Wt. of solution.	Wt. of residue.	Per cent of urea.
1	17	1.9543	0.0179	3.00
2	40	2.1796	0.0219	3.30
3	30	2.2749	0.0234	3.30
4	45	2.1554	0.0221	3.36

Average 3.24
Average of last three 3.32

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[1] *Ann.*, **248**, 235 (1888).

The last column is the ratio of the urea formed to that which would be formed by the complete conversion of the carbamate.

In order to approach this same equilibrium from the other side, a solution was prepared of the same total equivalent content, but containing in 8.292 g. of water 4.603 g. of carbamate and 0.593 g. of urea. The results obtained by heating this solution are given in Table III:

TABLE III.

Experiment.	Hrs. of heating.	Wt. of solution.	Wt. of residue.	Per cent of urea.
1	40	2.0505	0.0207	3.30
2	51	2.2081	0.0224	3.33
			Average	3.315

This result agrees well with that obtained from the other side, and we may take 3.31 as the final mean.

In order to calculate the equilibrium composition at any temperature, in particular for the standard temperature of 25°, it is necessary to know the equilibrium at two temperatures at least. As a second temperature, the boiling point of toluene was selected. The average temperature of the bath in the experiments was 110.7°. The equilibrium at this temperature was approached from pure carbamate, Table IV, and from carbamate with an excess of urea, Table V. At this temperature the reaction proceeds more slowly, about five days being required for the establishment of equilibrium:

TABLE IV.

Days of heating.	Per cent of urea.
7	2.08
8	2.18
10	2.04
Average	2.10

TABLE V.

Days of heating.	Per cent of urea.
7	2.18
8	2.10
Average	2.14

The two tables show satisfactory agreement, and 2.12% will be taken as the final mean.

An attempt was made to determin the equilibrium at a still lower temperature, namely in a bath of carbon tetrachloride, boiling at 77°. Tubes taken out for analysis from time to time showed an even lower reaction velocity than was to be predicted. At the end of 95 days of continuous heating a tube which originally contained pure carbamate gave 0.9% urea, while one which originally contained an excess of urea gave 1.1%. The true value must lie between these limits. We may calculate the equilibrium percentage at this temperature from the measurements at the two higher temperatures by means of the equation,

$$\ln X_2/X_1 = C(T_2-T_1)/(T_1T_2),$$

where X_2 and X_1 are the percentages of urea at the temperatures T_2 and T_1 and C is a constant, provided that the heat of the reaction does not change materially with the temperature.[1] We thus find from the measurements at 132° and 110.7° that $C = 1512$, and we may calculate the percentage of urea at any other temperature; thus we find at 77°, 0.944%, which lies between the limits 0.9% and 1.1% experimentally determined.

We might at once have proceeded to calculate from these data the equilibrium percentage of urea at 25°, were it not for a doubt which arose during the later part of the work as to the complete purity of the ammonium carbamate prepared by the method described above. It seemed probable that in drying this product it was not wholly freed from traces of alcohol and ether. This doubt led us to prepare more carefully, by another method, a similar solution which we shall call Solution B. This was made by passing carbon dioxide into strong aqueous ammonia until the solution showed on analysis equivalent amounts of ammonia and carbon dioxide. This solution contained 1 g. of carbonate to 1.56 g. of water and was, therefore, 4% less concentrated than Solution A. All of the essential data upon which our final calculations rest were carried out on Solution B.

Four determinations of the equilibrium in Solution B at 132° were made. No excess of urea was added. The results are given in the following table:

TABLE VI. (FINAL.)

Hours of heating.	Per cent of urea.
24	3.21
24	3.28
48	3.22
48	3.22
	Average 3.23%

The average for the somewhat stronger solution, A, was 3.31%. These two solutions are obviously so nearly the same in composition that the constant C of the van't Hoff equation, which we have used, is the same for both. We may therefore calculate the equilibrium percentage of urea for Solution B at 25°, and thus find it to be 0.180%. This is the value we shall use in our further calculations.

Determination of the Activities at 25° of the Several Constituents in the Equilibrium Mixture.

In the concentrated solution which we have been obliged to use, none of the laws of the perfect solution can be assumed to be valid, and there-

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[1] It may not be obvious that the van't Hoff equation is valid in a case of this kind, where some of the reacting substances are present in highly concentrated solution, but since the urea is present in such small amounts that its activity in this particular mixture may be considered proportional to its percentage, the formula may readily be shown to be correct.

fore for the further utilization of our data other experiments and somewhat complicated calculations are necessary.

The equation for the reaction which we are investigating may be written in various ways. For our purpose it will be simplest to write,

$$2NH_3 + CO_2 = CO(NH_2)_2 + H_2O.$$

The free energy change of this reaction in the equilibrium solution is, of course, zero.[1] If then we know the free energies of ammonia, carbon dioxide and water in this mixture, we know also that of urea. The free energies of the three former substances under conditions which have been chosen as normal conditions, have previously been determined by their reversible syntheses from the elements. Our next step, therefore, must be to determin the relation between the free energies of these substances in our equilibrium mixture and their free energies under normal conditions; in other words, we must determin the ratio of the activity of each of these substances in the equilibrium solution to its activity in the normal or standard state.

We will take water, carbon dioxide and ammonia, all in the gaseous state, at atmospheric pressure and at 25°, as our standards and under these conditions their activities will all be taken as unity. We will proceed now to the consideration of the activities of these substances in our equilibrium mixture.

The activity of each substance in the equilibrium mixture is, of course, equal to its activity in the gaseous space above the mixture and since, fortunately, all three of the substances in question are volatil, our problem may be solved by the determination of the vapor pressure of water, carbon dioxide and ammonia above the equilibrium mixture.

The method employed in these vapor pressure measurements consisted in bubbling a known volume of air through a series of saturation tubes containing the equilibrium Solution B, and analyzing the resulting gas mixture by means of a series of absorption tubes. The Solution B was left in the thermostat over night to ensure equilibrium between carbonate and carbamate. It was not considered necessary to add the small amount of urea which would be in equilibrium with the solution at this temperature. The first absorption tube contained a standard solution of hydrochloric acid. This was followed by a tube containing concentrated sulfuric acid and then by a double tube containing soda lime, followed by concentrated sulfuric acid. The three absorption tubes were weighed separately before and after the experiments. The gain in weight of the first two gave the weight of ammonia plus water. A titration of the contents of the first tube gave the weight of ammonia. The gain in weight of the final double tube gave the weight of carbon dioxide. A number of pre-

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[1] Several of the thermodynamic ideas here employed will be more fully explained in a paper by Lewis which is about to appear in THIS JOURNAL.

liminary experiments were carried out before the desired degree of precision was attained. Some of these were vitiated by the transference of a certain amount of spray into the absorption tubes. This trouble was avoided by the aid of plugs of cotton wool at the end of the chain of saturation tubes, but inside the thermostat. Since these preliminary measurements were all made with Solution A, we omit any further discussion of them. The results of the final experiments with Solution B, are given in Table VII:

TABLE VII.

Experiment.	Time of bubbling (minutes).	Wt. of absorbed gases (grams).			Partial pressures (mm.).		
		NH_3.	CO_2.	H_2O.	NH_3.	CO_2.	H_2O.
1	160	0.0382	0.0410	0.0214	33.0	13.7	17.5
2	160	0.0403	0.0417	[0.0155]	34.8	13.9	[12.7]
3	120	0.0398	0.0399	0.0224	34.4	13.3	18.3
4	120	0.0416	0.0402	0.0220	35.9	13.4	18.0
				Average	34.5	13.6	17.9

In each case 1206 cc. of air were drawn through and this volume must be corrected for the fact that the air was saturated with water vapor when first measured, but while passing through the saturation tubes contained water vapor, carbon dioxide and ammonia at the prevailing partial pressures. From the following data the true volume passing through the saturation apparatus was calculated to be 1265 cc. And this number was used in calculating the partial vapor pressures given in the table. The final values for the vapor pressures expressed in atmospheres are 0.0454 for ammonia, 0.0179 for carbon dioxide, and 0.0235 for water, and these numbers are the activities of the three substances in the equilibrium mixture at 25°, the activities at one atmosphere being taken as unity. The three gases concerned were assumed to obey the gas law. This assumption is not entirely correct, but sufficiently so for our present calculations.

Knowing then the activities of ammonia, carbon dioxide and water in the equilibrium mixture, we are now in a position to calculate the free energy of urea in that mixture. This calculation alone, however, would be of no great service; it is necessary to find the free energy of formation of urea in some standard state before our result can be made available for further useful calculations. We shall choose as the standard state in this case solid urea at atmospheric pressure.

Our next step, therefore, is to determin the activity of urea in the equilibrium mixture relative to the activity of solid urea. Of the various methods of accomplishing this result which suggested themselves, the most promising was one depending upon the determination of the distribution of the urea between the equilibrium mixture and some organic solvent. Ethyl acetate was chosen for this purpose.

Preliminary experiments showed that when Solution B containing the equilibrium amount of urea was shaken with ethyl acetate, too little urea went into the ethyl acetate layer to be determined by any analytical method. It seemed justifiable to assume, however, that the activity of the urea in Solution B (which for this purpose may be regarded as a simple solvent) is proportional to the concentration, up to the concentration of one mol. of urea to 2000 g. of solvent, and solutions of about this strength were employed in the distribution experiments.

It seemed that it would be a simple matter to determin first the distribution of the urea between Solution B and ethyl acetate and then the solubility of solid urea in ethyl acetate, thus obtaining the necessary data for the calculation. At first difficulties were encountered which were due to impurities in the ethyl acetate. This was in the first instance prepared for use by shaking with sodium carbonate solution, drying with calcium chloride and distilling: such treatment, however, proved inadequate. A pure product was finally obtained from Kahlbaum's C. P. ethyl acetate by shaking with potassium carbonate solution, then with about one-fifth its volume of water, and by distilling from above the aqueous layer. The upper layer of this distillate was dried roughly with anhydrous potassium carbonate, then fractionally distilled several times from phosphorus pentoxide.[1] Practically all of the final product distilled over within one or two-tenths of a degree of the true boiling point.

New difficulties now arose of a more fundamental character, for it soon became evident that the solubility of urea in ethyl acetate is enormously affected by the presence of water, indeed the solubility is, as we shall see, roughly speaking, proportional to the amount of water present. Now the ethyl acetate which was shaken with Solution B contained a considerable amount of water[2] and therefore can by no means be regarded as identical with dry ethyl acetate. It is evident, therefore, that what is important for our purpose is not the solubility of urea in dry ethyl acetate, but in that particular wet ethyl acetate which is in equilibrium with Solution B. The preparation of such a saturated solution, however, proved to be impossible experimentally, for when solid urea was shaken with wet ethyl acetate it produced two liquid phases, and the amount of water necessary to produce this phenomena proved to be just about the amount present in the ethyl acetate shaken with Solution B.

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[1] That this reagent removes all traces of alcohol as well as of water was shown by Young and Thomas, *J. Chem. Soc.* (*London*), 63, 1194 (1893).

[2] It was shown by analysis that no other substance except water was taken up by the ethyl acetate from Solution B. If, however, the shaking was prolonged for several hours the contact with the ammonium carbonate solution caused an appreciable hydrolysis of the ethyl acetate, and this vitiated many of the earlier experiments, which had therefore to be discarded.

It seemed desirable, therefore, to find the solubility of urea in ethyl acetate containing different amounts of water, from zero to the amount which causes the appearance of two liquid phases. The results are given in Table VIII:

TABLE VIII.

Grams water to 100 g. solution.	Grams urea to 100 g. solution.
0.000	0.080
0.652	0.148
1.112	0.198
1.638	0.296
1.677	0.308
2.006	0.328 2nd liquid phase suspected.
2.138	0.342 2nd liquid phase suspected.
3.234	0.343 2nd liquid phase noticeable.

If these results are plotted, we see that the solubility of urea is a continuous function of the water content up to 1.8% water, which proves to be the point where the second liquid phase appears.

We may extrapolate along the continuous course for a short distance and if we now determin the water content of the ethyl acetate shaken with Solution B, we may find from the plot the amount of urea which would dissolve in that liquid if the separation did not occur.

The determination of the content of water in a liquid such as ethyl acetate is by no means easy. The method which we adopted had the advantage of employing the same experimental technique that we were already using. It consisted in adding to a given weight of the wet ethyl acetate a definit weight of dry ethyl acetate and determining the solubility of urea in the mixture. By reference, then, to the curve obtained from Table VIII, the total amount of water present is found. After some preliminary experiments, which showed the approximate composition of the ethyl acetate, the following careful experiment was made: Ethyl acetate was shaken 30 minutes with Solution B and 47.65 g. of the wet ester were added to 29.89 g. of the dry. The solubility of urea in this mixture was found in two experiments to be 0.204 and 0.203 gram urea in 100 grams of the saturated solution. This solubility corresponds to 1.15% water in the mixture, or 1.87% in the original wet ethyl acetate. The solubility of urea in the latter solution is found by reference to the plot to be *0.36 g. to 100 g. solution.*

In the meantime, numerous experiments were made on the distribution of urea between the wet ethyl acetate and solution B. Only the results of the last two in which Solution B and the pure ethyl acetate were used need be given. They are contained in Table IX:

TABLE IX.

Experiment.	Time of shaking (minutes).	Conc. urea in aqueous layer (g. urea to 100 g. solution).	Conc. urea in ester layer (g. urea to 100 g. solution).
1	30	3.411	0.0226
2	25	3.435	0.0214

In Experiment 1, there was initially an excess of urea dissolved in the ester; this was not the case in Experiment 2. It is apparent, therefore, that equilibrium was not quite reached from either side, but the average of the two values must be close to the true value, and nearer than if contact between the solvents were prolonged, with consequent hydrolysis of the ester. This average gives the partition coefficient:

$$\frac{\text{Conc. urea in aqueous layer}}{\text{Conc. urea in ester layer}} = 155.8.$$

Our previous equilibrium measurements have shown that if Solution B were brought to equilibrium at 25°, 0.180% of urea would be formed, or 0.0541 g. urea to 100 g. of solution. Therefore, ethyl acetate if shaken with Solution B containing this equilibrium amount of urea would contain $0.0541 \div 155.8 = 0.000347$ g. of urea to 100 g. of ester solution. Consideration of the percentage of water found present in ethyl acetate shaken with Solution B and reference to the curve of solubilities of urea has shown that solid urea is soluble in this ester at 25° to the concentration of 0.36 g. to 100 g. of solution. Hence the activity of the urea in the equilibrium mixture in terms of that of solid urea as unity is $0.000347 \div 0.36 = 0.000965$.

The Free Energy of Solid Urea.

The activities of all the constituents that enter into the equilibrium now being known, the free energy change that accompanies the reaction represented by the equation,

$$CO_2 \text{ (gas)} + 2NH3 \text{ (gas)} = CO(NH_2)_2 \text{ (solid)} + H_2O \text{ (gas)},$$

may be immediately calculated.

If a_1, a_2, a_3, and a_4 represent the activities respectively of CO_2, NH_3, $CO(NH_2)_2$ and H_2O in the equilibrium mixture, then for the free energy change under the normal conditions we may write

$$\Delta F = -RT \ln a_3a_4/a_1a_2^2.$$

We have found $a_1 = 0.0179$, $a_2 = 0.0454$, $a_3 = 0.000965$, $a_4 = 0.0235$, hence $\Delta F = -RT \ln 0.615 = 288$ cal.

If we choose, we may refer the free energy to liquid water by using the equation:

$$H_2O \text{ (gas)} = H_2O \text{ (liquid)}; \Delta F = -RT \ln 0.031 = -2060 \text{ cal.},$$

since the vapor pressure of water at 25° is 0.031 atmospheres. Combining this equation with the preceding, gives

$$CO_2(g.) + 2NH_3(g.) = CO(NH_2)_2(s.) + H_2O \text{ (l.)}; \Delta F = -1772.$$

Since the free energies of CO_2, NH_3 and H_2O are all known, we are now in a position to calculate the free energy of formation of solid urea. However, as some of these values are now being submitted to a systematic revision, we shall not make this simple substitution at this point.

The Free Energy of a Molal Solution of Urea in Water.

Our next step is to determin the relative activity of urea in the solid state and in dilute aqueous solution. It was at first hoped that this could be done very simply by determining the solubility of urea in ethyl acetate and the coefficient of distribution of urea between ethyl acetate and water. But the difficulties already described become even more serious in this case. What we wish to determin is, of course, the solubility of urea in the same ethyl acetate which is used in the distribution experiments, that is, in the ester layer which has been shaken with nearly pure water. A determination of the water content of this wet ester was carried on as before by diluting the wet ester with dry ester and measuring the solubility of urea in the mixture. Of the wet ester, 33.23 g. were added to 44.36 g. of dry ester and the solubility of urea (g. urea to 100 g. solution) was determined in two experiments, giving (*a*) 0.2624 g. and (*b*) 0.2615 g. Average, 0.262 g. By consulting the curve mentioned previously, we thus find that the ethyl acetate saturated with water at 25° contains 3.5% of water. The same result was obtained by a wholly different method, namely, by determining directly the amount of ethyl acetate in the wet ester by saponification with alcoholic potash. Two sets of determinations gave for the water content 3.45% and 3.56%, average 3.5%.

Since the solubility of urea can only be determined directly up to 1.8% water content, the extrapolation to 3.5% water content by means of the curve expressing the data of Table VIII cannot be very accurate. This extrapolation gives as the solubility of urea in the ester of 3.5% water content, approximately 0.7 g. urea to 100 g. of solution.

The final experiments upon the distribution of urea between water and the wet ester are as follows:

	Time of shaking (minutes).	Conc. urea, aqueous layer. (g. to 100 g. sol.).	Conc. urea, ester layer. (g. to 100 g. sol.).
1	135	5.80	0.048
2	135	5.80	0.050
			Average 0.049

This gives for the distribution coefficient

$$\frac{\text{Conc. urea in aqueous layer}}{\text{Conc. urea in ester layer}} = 118.$$

A molal solution of urea (1 mol. to 1000 g. H_2O) would contain 5.66 g. per 100 g. solution and would therefore be in equilibrium with an ester solution containing 0.0478 g. urea to 100 g. solution. The solubility of urea in the same wet ester is 0.7 g. to 100 g., and therefore the ratio of the activity of solid urea to that of urea in molal aqueous solution is 14.6.

This value, however, owing to the magnitude of the extrapolation involved in its calculation, was distrusted and it was therefore decided to make an entirely new determination of this ratio. This was done in an indirect way through a study of the vapor pressure of water at 25° over various aqueous solutions of urea. The results are given in Table X. The measurements were made by passing a known volume of air through several tubes containing a solution of urea and collecting the water thus evaporated in sulfuric acid; the usual corrections were made:

TABLE X.

Mol fraction of water.	Vapor pressure (mm. mercury).	Average vapor pressure.	Vapor pressure H_2O ÷ Mol fraction H_2O.
1.000	...	23.55[1]	23.55
0.926	21.53	21.50	23.2
..	21.47	...	...
0.890	20.48	20.55	23.1
...	20.61	...	...
0.843	19.56	19.51	23.2
....	19.46	...	...
0.797	18.69	18.70	23.5
...	18.71	...	...

These experiments were not carried out with the highest degree of accuracy, but they show that the vapor pressure of the water is very nearly proportional to its mol fraction. In the most concentrated, and, therefore, the most significant solution, the ratio is identical with the vapor pressure of pure water.

In the other cases, the discrepancies are larger than the estimated experimental error. Whether these discrepancies are real can only be determined by further experiment. At present we may say that the vapor pressure of the water is very nearly, if not strictly, proportional to its mol fraction. In other words, we are dealing with a perfect solution, and it is therefore a necessary consequence that the activity of the urea is proportional to its mol fraction.

The most concentrated of the solutions used is not far from a saturated solution. By means of solubility experiments, the saturated solution at 25° was found to contain 0.242 mol fraction of urea. The mol fraction in a molal solution is $1 \div 56.5 = 0.0177$. The ratio of the activity in saturated and in molal solution is, therefore, $0.242 \div 0.0177 = 13.7$. But the activity in the saturated solution is identical with that of solid urea. We therefore find for the activity ratio between solid urea and molal solution 13.7 as against 14.6 by the other method. The second method is probably the more reliable and we may choose 14.0 provisionally as the weighted mean.

We may therefore write:

$$CO(NH_2)_2(s.) = CO(NH_2)_2\ (molal);\quad \Delta F = -RT \ln 14 = -1562.$$

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[1] Landolt and Börnstein.

Combining this with the preceding equation,

$$CO_2(g.) + 2NH_3(g.) = CO(NH_2)_2(s.) + H_2O(l.);\ \Delta F = -1772,$$

gives

$$CO_2(g.) + 2NH_3(g.) = CO(NH_2)_2\ (molal) + H_2O(l.);\ \Delta F = -3334.$$

The Free Energy of Formation of Ammonium Cyanate.

In the experiments of Walker and Hambly,[1] of Walker and Kay,[2] and of Fawsitt,[3] the equilibrium between urea and ammonium cyanate in dilute aqueous solution has been determined. From their several observations the percentage of 0.1 molal urea converted into cyanate is 6.6, 6.2, 6.5; average, 6.5%. Assuming the ammonium cyanate in this very dilute solution to be completely dissociated, we have for the equilibrium constant in the reaction $CO(NH_2)_2 = NH_4^+ + CNO^-$.

$$K = \frac{(0.0065)^2}{0.0935} = 0.00045.$$

The heat of the reaction as given by Walker[4] is 7500 cal. Whence, applying the van't Hoff equation, we find at 25° $K = 0.000035$. Hence, $\Delta F = -RT \ln K = 6100$, where ΔF refers to normal conditions, that is to the reaction,

$$CO(NH_2)_2\ (molal) = NH_4^+\ (molal) + CNO^-\ (molal) + H_2O_1(l.);$$
$$\Delta F = 2766.$$

How we may proceed from this equation to calculate the free energy of formation of hydrocyanic acid and other important compounds will be discussed in another paper.

[Contribution from the Chemical Laboratory of the University of Michigan.]

ON TRIPHENYLMETHYL. XXI. QUINOCARBONIUM SALTS OF THE HYDROXY-XANTHENOLS.

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[1] *J. Chem. Soc.*, **67**, 746 (1895).

[2] *Ibid.*, **71**, 507 (1897).

[3] *Z. physik. Chem.*, **41**, 601 (1902).

[4] *Ibid.*, **42**, 207 (1902).

[5] This investigation was presented by Mr. West to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.