molecular weight chain compounds, be they in aqueous or in nonaqueous solution. Bungenberg de Jong regarded coacervates as macromolecular aggregates in which a considerable amount of solvent is immobilized or occluded inside the loops of molecular skeins. This idea also gets some support from the work of Alfrey, Bartovics, and Mark (*5*) on the solutions of polymers in good and bad solvents. It has been shown by these authors that the molecules of polymeric chain in the dissolved state in good solvents take up an extended structure. As the solvent character is rendered more and more unfavorable by the addition of some precipitant the polymer chain becomes more and more coiled up. So it is expected that at the time of separation the extensively coiled-up polymer molecules will carry along with them considerable quantities of occluded solvents immobilized inside the loops of molecular skeins. The separation of coacervates therefore follows from the idea of flexibility of the chain molecules and the solvent immobilization inside the coiled-up molecules. It follows as a corollary from these viewpoints that if a molecule separates out of the solution in its extended configuration it will give a solid product, whereas if it separates in the coiled-up state coacervation will take place.

In order to test this point experiments were planned taking into consideration the present conception of the change in the molecular configuration of polyelectrolytes under different working conditions (*6*). The best-known example of the coacervation phenomenon is the separation of gelatin from aqueous solution by the addition of alcohol. Gelatin is a protein that contains a number of carboxyl and amino groups distributed along the chain. When sodium hydroxide is added to a gelatin solution some of the COOH— groups are converted into COONa, which in its turn undergoes dissociation into COO^- and Na^+. The protein chain is thereby left negatively charged, and the repulsion between the similarly charged COO^- groups on the same chain will cause the protein molecule to take up an extended configuration. If alcohol is added to the solution, precipitation will take place more or less in the solid form. Similarly, when HCl is added to the solution, the NH_2 groups will be converted into hydrochloride, which will also undergo dissociation, leaving the extended chain positively charged, and the precipitation will lead to solid separation rather than coacervates.

If, however, sufficient sodium chloride is added to solutions of gelatin hydrochloride or sodium gelatinate at different pH's, the dissociation of sodium gelatinate or gelatin hydrochloride will be considerably suppressed, owing to common ion effect; the negative and positive charge centers will be neutralized, and the molecules will take up a less extended, average coiled-up structure. Addition of alcohol to such solutions will lead to coacervation rather than solid separation. The results of precipitation of gelatin from aqueous solution at different pH's by alcohol in the presence and in the absence of sodium chloride are summarized in Table 1.

TABLE 1

PRECIPITATION OF GELATIN BY ALCOHOL

Without NaCl		With NaCl	
pH	Nature of the precipitate	pH	Nature of the precipitate
9.6	Granular solid	9.8	Viscous liquid
8.7	Hard gel	8.5	" "
7.1	Viscous liquid	7.5	" "
5.5	" "	5.7	" "
4.6	" "	4.0	Setting to gel
3.5	Granular solid	3.0	" " "
2.6	" "		

It is evident from Table 1 that in the absence of sodium chloride gelatin separates as granular solid both at higher pH's (where the conversion of gelatin to its sodium salt is nearly complete) and at lower pH's (where gelatin exists as hydrochloride) by the addition of alcohol, whereas in presence of sodium chloride coacervation takes place at all pH's (pH adjustments were done in these cases either by the addition of NaOH or HCl).

In the case of precipitation of gum arabic from aqueous solution with alcohol, similar results have been obtained. At higher pH's separation takes place in the solid form; and in the presence of sodium chloride at those pH's separation of oily droplets (visible under the microscope) takes place. The droplets gradually agglomerate to a sticky, jellylike mass.

These observations, along with the analysis set forth, therefore lend further support to the Bungenberg de Jong explanation of the coacervation phenomenon as due to separation of coiled-up molecules with a considerable amount of immobilized solvent inside the loops of molecular skeins.

References

1. KRUYT, H. R. *Kolloid-Z.*, **50**, 39 (1930).
2. BUNGENBERG DE JONG, P. J., *et al. La Coacervation.* Paris: Herman (1936); *Proc. Acad. Sci. Amsterdam,* **44**, 1099 (1941).
3. DOBRY, A. *Rev. can. biol.*, **1**, 353 (1942).
4. BUNGENBERG DE JONG, P. J. In H. R. Kruyt (Ed.), *Colloid Science,* Vol. 2. Houston: Elsevier, 248 (1949).
5. ALFREY, T., JR., BARTOVICS, A., and MARK, H. *J. Am. Chem. Soc.,* **64**, 1667 (1942).
6. FUOSS, R. M. *Science,* **108**, 545 (1948).

Manuscript received October 17, 1951.

Effect of Heat on the Properties of Urea at its Melting Point

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The melting point of pure urea is 132.7° C as given in the literature (*1*). If urea is heated above its melting point at temperatures from 150° to 200° C, biuret, tricyanurea, and several other products are formed successively. Some of them are generally considered to represent polymerization products of the single

urea molecule. Most of these products are well identified and described in the literature.

Urea was originally considered to be a diamide of carbonic acid. Lately Degering (*2*), as well as Werner (*3*), explained the polymerization tendency of urea as being due to a more reactive form of urea. Several formulas were assigned to this active form. Brauch and Calvin (*4*) explained the presence of an activated form of urea as follows: the C—N distance in the urea molecule was determined to be 1.37 A, whereas in aliphatic amines this distance normally amounts to 1.47 A. The difference in these values may be due to the presence of two modifications of normal urea. Freudenberg (*5*) admits the possible presence of isomorphous forms in urea but the iso-urea could not be detected by x-ray spectrography as practiced at the time of his investigations.

Since this work was carried on at temperatures considerably above the melting point of urea, it was proposed to study the effects on urea when its temperature was varied slightly above and below the melting point.

The following experiments were done with urea, reagent grade. Its melting point was 132.2° C, and its nitrogen content was 45.62%, as determined at the beginning of the tests. Five-g samples, in either open or sealed glass tubes, were submerged in an oil bath which had a constant temperature control. Between each heating cycle, the sample was removed from the oil bath and allowed to solidify in air before it was reheated. After each series of melting cycles the sample was analyzed (Table 1). A Kofler Micro Hot

TABLE 1

UREA REPEATEDLY HEATED AT THE MELTING POINT

Times melted and solidified	Mp(°C)	pH	N_2 content (%)	Solubility in	
				H_2O	Abs alcohol
Urea	132.2	6.8	45.62	.6255	.0871
" 10	124.4–129.5	7.1	45.04	.6543	.0972
" 20	122.4–123.0	9.0	44.22	.6625	.0996
" 30	117.8–118.1	9.1	45.84	.6682	.1000
" 40	112.5–113.4	9.1	46.01	.6740	.0937
" 60	112.7–112.9	7.1	46.15	.6753	.0925

Stage unit was used to obtain temperature readings, which were held constant for 2 hr during the melting process. A lowering of the melting point to approximately 112.5° C will be noted as the most significant change in the urea during this investigation. After 40 melting cycles, however, the melting point became fairly stable.

Samples of urea and iso-urea crystals were powdered to pass through a 300-mesh screen and then worked into thin-walled glass (Keesom) tubes which had a diameter of 0.5 mm or less. The tubes were sealed to prevent absorption of water vapor. A 57.3-mm Debye powder camera with 0.5-mm pinholes was used to obtain the x-ray diffraction patterns. Filtered

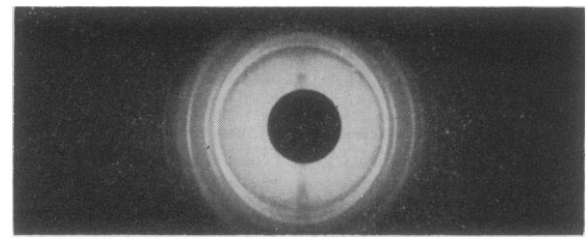

FIG. 1. Urea.

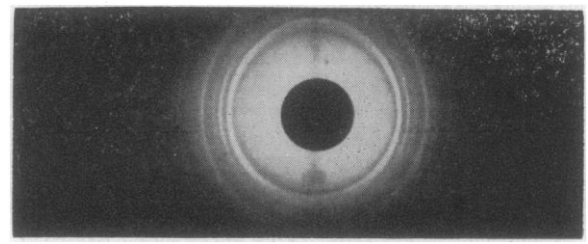

FIG. 2. Iso-urea.

Cu-radiation at 40 kv and 15 ma gave readable lines with 1-hr exposures.

The "*d*" values (spacings of the atomic planes) for the x-ray diffraction lines of the urea were found to be in close agreement with the ASTM values of this substance, but the "*d*" values for the iso-urea x-ray diffraction lines differed somewhat from those for the urea lines. The iso-urea pattern (Figs. 1, 2) shows a diffraction line (third from the center) which is not present in the urea pattern. This line becomes progressively stronger with an increased number of melting operations, and another line farther from the center of the iso-urea pattern becomes progressively weaker with an increased number of melting operations. There are a number of the other lines on the two patterns which do not "match" either in "*d*" values or intensities, so a difference in structure is to be inferred.

Urea is generally considered to be a stable compound. It has been demonstrated experimentally that the stability of urea or its uniformity is questionable and that a new and stable compound is being formed during this treatment as shown by the x-ray diffraction patterns and the more constant melting point. This investigation is a contribution to the theory advanced by Degering and others that it should be possible to prove experimentally that urea consists of isomorphous compounds or may be transformed into isomorphous compounds from its normal state by repeated melting and solidification.

References

1. *Beilsteins Handbuch der Organische Chemie.* Vol. 3, 4th ed. Berlin: J. Springer, 42 (1921).
2. DEGERING, E. F. *Organic Nitrogen Compounds.* Cincinnati: Swift, 193 (1942).
3. WERNER, E. *Chemistry of Urea.* London: Longmans, Green, 25 (1923).
4. BRANCH, G. E. K., and CALVIN, M. *Theory of Organic Chemistry.* New York: Prentice-Hall (1941).
5. FREUDENBERG, K. *Stereochemie.* Vienna: F. Deuticke (1933).

Manuscript received November 13, 1951.