Summary.

In this paper are described careful determinations of the compressibilities of certain liquid hydrocarbons, alcohols, amines, esters, and organic halides. The results, taken in connection with several others previously published, are tabulated in such a way as to show that in general the greater the compressibility of a substance, the greater is its decrease with increasing pressure. Further, it is pointed out that this very general rule is just what one might predict from the theory of compressible atoms. The new data will shortly be compared, in a following paper, with many other physical properties of the liquids in question.

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THE EQUILIBRIUM BETWEEN AMMONIUM CARBONATE AND AMMONIUM CARBAMATE IN AQUEOUS SOLUTION AT 25°.

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The substance known as carbamic acid, NH_2COOH, although hitherto little studied, is interesting not only because it is the first member of an important series of organic acids, but also because its ammonium salt always occurs in considerable amount in aqueous solutions of ammonium carbonate. The determination of the equilibrium in such solutions is an important step in the investigation of the properties of carbamic acid.

In the year 1885, Fenton[1] made measurements on this equilibrium, his method of analysis being based on the difference in action of alkalin hypochlorite and hypobromite solutions toward ammonium and amino groups, previous experiments[2] having shown that the hypochlorite solution liberates nitrogen from ammonium groups only, while sodium hypobromite acts on both ammonium and amino groups. In the present case, however, owing to the rapidity with which the carbamate and carbonate are transformed into one another under ordinary conditions, it appeared unlikely that the results obtained by Fenton could have much more than qualitative significance. A determination by some other method of analysis seemed therefore desirable.

It is well known that solutions of calcium or of barium salts do not produce precipitates in freshly prepared solutions of ammonium carbamate, but that the mixtures become turbid on standing for a short time at room temperature, and, if kept neutral or slightly alkalin, precipitation as carbonate is soon completed. A series of experiments involving the precipitation and determination together of the carbonate and carbamate by addition of cold barium hydroxide solution drew at-

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[1] *Proc. Roy. Soc. London,* **39**, 386 (1885).

[2] *J. Chem. Soc.,* **35**, 12 (1879).

tention to the slowness with which the equilibrium between these salts adjusts itself at low temperatures, and suggested the possibility of using the reaction for their separate determination.

If an ice cold solution containing both ammonium carbonate and carbamate is treated with an excess of an ice cold solution of barium hydroxide, or of barium chloride containing a small amount of ammonia, and immediately filtered, the filtrate, if kept cold, will remain clear for as long as one-half hour.

A difficulty in applying this method of separation was encountered when the attempt was made to wash free from carbamate the first precipitate of barium carbonate, within the allowable time limit, precipitation in the cold and immediate filtration being both unfavorable to rapid washing. This difficulty was overcome when porous alundum ware crucibles were employed. With these and by the use of Gooch funnels and a filter pump, filtration and washing were carried out rapidly, and the filtrates usually remained perfectly clear for some minutes after the washing was completed.

The solutions tested were made from ammonium carbamate. Two somewhat dilute solutions and one concentrated solution were examined. The dilute solutions were made up by weight to be 0.2 and 0.05 molal. The concentrated solution was made by dissolving 1 g. of the carbamate in 1.5 g. of water. Suitable quantities for analysis were sealed up in glass tubes, and placed in a thermostat at 25° for sufficient time (12–24 hours) to insure equilibrium. On removal the tubes were thrust into ice water and then opened, or in other cases immediately opened and drained onto ice. Ice cold barium chloride solution containing a small amount of ammonia was immediately added, and the precipitate washed in the open air, the temperature of which was near the freezing point. The filtrates were collected in Erlenmeyer flasks, which were subsequently stoppered and warmed on a water-bath to precipitate completely the carbamate as barium carbonate. The washed precipitates were titrated in the crucibles with standard hydrochloric acid.

Omitting the experiments made before the alundum crucibles were adopted, the results obtained are as shown in the following table:

	0.1 N HCl to titrate precipitate from			Mol. per cent of total salt as	
Wt. Sample, g.	Carbonate. cc.	Carbamate. cc.	Total molal conc. calculated from columns 1, 2, 3.	Carbonate.	Carbamate.
38.32	34.46	3.93	0.0501	89.9	10.1
39.02	35.12	3.87	0.0500	90.3	9.7
13.31	41.64	9.82	0.195	80.8	19.2
12.16	38.19	9.06	0.196	80.8	19.2
2.097	80.94	125.2	1 gram carbamate to 1.5 grams water	39.15	60.85
1.838	70.98	110.0		39.20	60.80
2.060	80.49	123.8		39.20	60.80

The results of Fenton for the molal concentrations 0.277, 0.185, 0.138, 0.111, are respectively 74.87, 79.62, 84.47, 91.56 per cent carbonate. These agree with ours only in the order of magnitude.

If the reaction be written $NH_2.CO.ONH_4 + H_2O = (NH_4)_2CO_3$, then in dilute solution the ratio of carbamate to carbonate might be expected to remain constant. But this equation takes no account of ionization and hydrolysis. We have no information regarding the strength of carbamic acid. If, as might be presumed, it is a very weak acid, then its ammonium salt would be almost completely hydrolyzed; that is, would consist essentially of free ammonium hydroxide and carbonic acid. The ammonium hydroxide from this source would, to a large extent, prevent the hydrolysis of the ammonium carbonate and the reaction would best be written in the form

$$NH_4OH + NH_2.CO.OH = 2NH_4^+ + CO_3^{--}.$$

In other words, we should expect, if these assumptions be correct, the square of the carbamate concentration to be roughly porportional to the cube of the carbonate concentration. This is approximately the case, for if we assume this law and calculate from the percentage of carbonate in 0.2 molal, the percentage in 0.05 molal solution, the result is 88.5%, while the observed was 90.1%.

At present data are lacking for a more careful consideration of this problem. We hope, especially through the study of the conductivity of freshly prepared ammonium carbamate solution, to obtain more definit evidence concerning the strength of carbamic acid.

A SPECTROGRAPHIC STUDY OF TELLURIUM.

By Wm. L. Dudley and E. V. Jones.

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Historical.

In 1869, Mendeléeff,[1] in announcing the Periodic Law, pointed out that the atomic weight of an element can sometimes be corrected as soon as its properties are known, and he said that the atomic weight of tellurium must be not 128, as it was then given, but 123 to 126. This statement at once suggested a problem which challenged the attention of a number of chemists, and has since been the subject of many researches. Various theories have been advanced to explain the anomalous position of tellurium in the periodic system. Tellurium, from a consideration of its general properties, falls into group 6, Series 7, of the periodic table. Its atomic weight, however, now given as 127.5, is higher than that of iodine, which is found in group 7, series 7, with an atomic weight of 126.92, which fact is out of harmony with the principles upon which the periodic table was

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[1] *Ber.*, **13**, 1799.