various types of building materials, of different classes of volatile liquids by nitro-cotton, and should be applicable to some hydration phenomena and even to determination of molecular weight in small quantities of solutions.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY OF THE UNITED STATES DEPARTMENT OF AGRICULTURE]

THE THERMAL DISSOCIATION OF SODIUM CYANIDE

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It has been recently shown[1] that the fixation of nitrogen as cyanides, usually represented by the equation,

$$Na_2CO_3 + N_2 + 4C \rightleftharpoons 2NaCN + 3CO \qquad (1)$$

takes place, at least to a large extent, through the following series of reactions.

$$Na_2CO_3 \rightleftharpoons Na_2O + CO_2 \qquad (2)$$
$$(C + CO_2 \rightleftharpoons 2CO) \qquad (3)$$
$$Na_2O + C \rightleftharpoons 2Na + CO \qquad (4)$$
$$2Na + 2C \rightleftharpoons Na_2C_2 \qquad (5)$$
$$Na_2C_2 + N_2 \rightleftharpoons 2NaCN \qquad (6)$$

The "over-all" equilibrium represented by Equation 1 was studied by Ferguson and Manning[2] and later by Ingold and Wilson[3] with somewhat different results. A few measurements were made in this Laboratory in conjunction with the present investigation and the results were found to agree more closely with those of Ingold and Wilson. It is, therefore, believed that the relation which they deduced for the variation in the composition of the Na_2CO_3-NaCN melt with the composition of the gas phase is at least fairly accurate. It will be seen, however, that the study of this "over-all" equilibrium does not give us as much information on the state of the system as would be desirable if the intermediate substances such as sodium oxide, sodium carbide or sodium are present at equilibrium in significant amounts.

It has been found that for a given ratio of nitrogen to carbon monoxide in the gases, the ratio of sodium cyanide to sodium carbonate in the molten phase increases rapidly with increasing temperature, so that according to the equation of Ingold and Wilson,

$$\log\left(\frac{x^2}{1-x}\cdot\frac{P^3_{CO}}{P_{N_2}}\right) = 23.91 - \frac{31738}{T}$$

the conversion of carbonate to cyanide should be 95% complete when the gas phase is 75% carbon monoxide and the temperature 1100°. It might,

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[1] THIS JOURNAL, **47**, 1932 (1925).

[2] Ferguson and Manning, *J. Ind. Eng. Chem.*, **11**, 946 (1919).

[3] Ingold and Wilson, *J. Chem. Soc.*, **121**, 2278 (1922).

therefore, be concluded that the fixation of nitrogen as cyanide should be carried out at higher and higher temperatures, when retort materials capable of withstanding those conditions are available, in order to take advantage of the shifting of the equilibrium toward cyanide. Before this conclusion can be justified, however, it is necessary to inquire whether at these higher temperatures intermediate compounds appearing in the above series of reactions, such as sodium oxide, metallic sodium and sodium carbide which are not directly involved in the equilibrium of Equation 1, are present in such quantity as to represent a considerable fraction of the sodium in the system.

It has been reported both by Ferguson and Manning and by Ingold and Wilson that at the temperatures at which their studies were made, 850–1000°, the concentration of sodium oxide was very small. Since the formation of sodium cyanide from sodium oxide, carbon and nitrogen is an endothermic reaction, it is to be expected that the proportion of oxide to cyanide in the melt will be even less at higher temperatures and, therefore, negligible at all temperatures above 850°. That leaves still to be determined to what extent sodium carbide and metallic sodium appear in the system at various temperatures. This problem has been attacked in the present investigation by attempting to determine the concentrations of these substances in the gas phase in equilibrium with a melt of pure sodium cyanide. From the standpoint of the study of the fixation of nitrogen as cyanide by a charge of sodium carbonate, carbon and iron, it would be useful to have such measurements on melts containing carbonate and cyanide as well as upon pure cyanide, but the experimental difficulties in the study are so great that the work has not been extended to that point.

It has apparently been invariably assumed in the literature that sodium cyanide is perfectly stable toward heat. The patent literature abounds with suggestions that sodium cyanide be distilled either during its formation or as a separate purification step. In the present paper, it will be shown that the assumption is not justified—that the vapor phase over sodium cyanide at relatively high temperatures is in fact far from being pure sodium cyanide. It had been hoped that the partial pressures of sodium, sodium carbide and sodium cyanide could be measured accurately enough so that equilibrium constants could be assigned for the equilibria of Reactions 5 and 6. Actually, it has not been found possible to obtain sufficiently reproducible results to permit a very satisfactory calculation of these equilibrium constants. It is believed, nevertheless, that a condensed statement of the results obtained will be of considerable interest, in that they do demonstrate the fact of the thermal dissociation of sodium cyanide and they show the approximate extent to which dissociation occurs. The difficulties which have prevented a more accurate determination of equilibrium constants will appear as the experiments are described.

Preparation of Pure Sodium Cyanide

It was desired to have for these experiments a supply of cyanide of higher purity than that available on the market, the best of which was found to contain at least 2 or 3% of non-cyanide alkali. Since the preparation of this compound in a high degree of purity is somewhat difficult, it appears worth while to describe the method which was finally evolved after considerable study.

Briefly, the method used is (1) to prepare pure liquid hydrogen cyanide and a solution of pure sodium hydroxide in absolute alcohol; (2) to pour the liquid hydrogen cyanide in slight excess (the success of the method depends on having an excess) into the sodium hydroxide solution (of a concentration of 40 g. per liter or less) which is cooled in an ice-bath and allow to stand for some hours, the flask containing the mixture being tightly stoppered. Since sodium cyanide is only slightly soluble in alcohol, the crystals separate from the solution as the reaction continues. When the reaction is complete, the supernatant liquid is decanted from the crystals and the crystals are washed two or three times by decantation with absolute alcohol. Finally, the crystals are transferred to a filter and after the bulk of the liquid is drained off, they are transferred to a vacuum desiccator containing phosphorus pentoxide by which practically all of the water is removed. The last trace of moisture is expelled by drying at 110° and finally fusing in a hydrogen or helium atmosphere. Throughout the preparation, care must be taken to exclude carbon dioxide. The flask for the sodium hydroxide solution is filled with air free from carbon dioxide before the solution is filtered into it and all of the washing and filtering of the crystals is done under a large inverted funnel through which a stream of air free from carbon dioxide is forced.

The method employed for the generation of hydrogen cyanide was that described by Wade and Panting,[4] according to which a 1:1 solution of sulfuric acid is allowed to drop onto solid sodium cyanide.

The hydrogen cyanide was dried by passing through a calcium chloride tube kept at 35° and condensed by passing through a cooling coil and into a receiver surrounded by an ice-salt freezing mixture at —15° to 0°.

The pure sodium hydroxide solution was at first prepared by dissolving metallic sodium in alcohol containing water equivalent to the sodium dissolved. It was found, however, that a quite pure solution could be obtained by dissolving a good grade of sodium hydroxide sticks in absolute alcohol and filtering. Sodium carbonate which is the chief impurity in the sticks is practically insoluble in alcohol.

In a typical experiment, 50 cc. (35 g. —10% excess) of liquid hydrogen cyanide was added to 1200 cc. of sodium hydroxide solution containing 47 g. of sodium hydroxide. The product after being dried and fused contained 99.95% sodium cyanide, as determined by the Lundell-Bridgman method.[5] Several lots of cyanide have been prepared by this method, each of about 50 to 60 g. and all of practically 100% purity.

Apparatus and Method for Measurement of Dissociation

The method used in these experiments was, briefly, to pass a known volume of gas at a slow rate over sodium cyanide at a measured temperature

[4] Wade and Panting, *J. Chem. Soc.*, **73**, 255 (1898).

[5] Lundell and Bridgman, *J. Ind. Eng. Chem.*, **6**, 554 (1914).

and afterward to determine the quantities of decomposition products carried by the gas.

In the majority of the experiments, an inert gas, helium, was used for this purpose rather than nitrogen, since (1) the amount of decomposition would be larger in the inert gas (nitrogen, being a product of the dissociation, should repress the dissociation) and (2) it was thought that it might not be possible to determine accurately the composition of the alkaline sublimate (sodium cyanide, sodium, sodium carbide) in which case the determination of the extent of dissociation would have to rest principally on the amount of nitrogen produced by the dissociation, which could not easily be determined if nitrogen were used as the flushing gas.

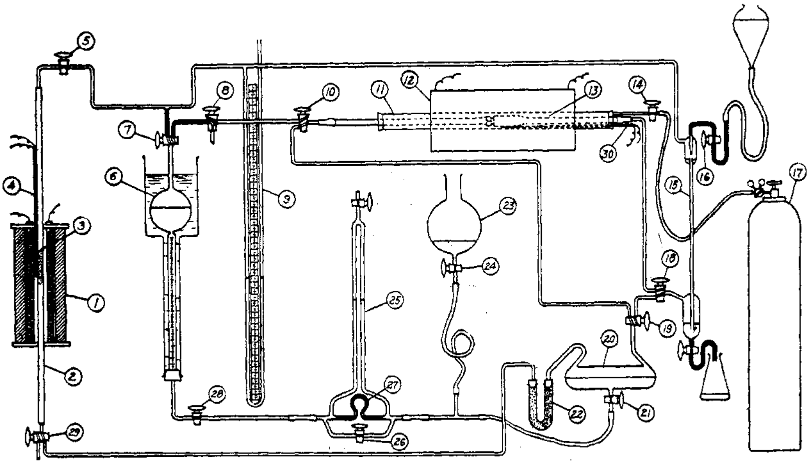

Fig. 1.—Apparatus used in the decomposition of sodium cyanide.

The steps in a typical experiment were (1) the purification of helium by circulation over powdered magnesium at 625°; the tank helium used contained about 5% of nitrogen and this was the only appreciable impurity; (2) the passage of purified helium at a rate varying from 2.5 to 7 cc. per minute over heated sodium cyanide; (3) analysis of the helium passed for nitrogen and of the sublimate which condensed from the gases as they cooled, for total alkalinity, cyanide and carbide.

A diagrammatic sketch of the apparatus is shown in Fig. 1; 12 is the cyanide decomposition furnace and 13 the element of the apparatus containing the decomposing sodium cyanide. The design of this apparatus has been previously described.[6] It is constructed of Monel metal and consists essentially of a central cylindrical charge chamber and inlet tube permanently welded into one end of the charge chamber and an outlet which is attached to the other end by means of a special joint which can be made gas

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[6] THIS JOURNAL, 48, 140 (1926).

tight and yet is capable of being detached following its subjection to a high temperature. The apparatus used in this study was larger than that previously described, the Monel charge chamber being about 1.6 cm. × 7 cm. The decomposition element was surrounded by the quartz jacket 11, which was kept filled with helium. The temperature was measured by a Chromel-Alumel thermocouple placed in a groove in the side of 13, the junction being at about the point where the outlet tube of 13 was connected. The temperature measured at the inlet end of the central enlarged portion of 13 containing the sodium cyanide was about 15° to 20° lower, so that there is an uncertainty of perhaps 10° or slightly more in the actual temperature of the sodium cyanide.

The furnace and magnesium tube for removing nitrogen, either in the purification of helium or in the analysis of the gas for nitrogen after an experiment, are shown at 1. In general, about six hours' circulation of the gases through the heated magnesium was required for complete removal of nitrogen. During this time, a given element of gas passed through the magnesium about 40 times. In order to insure complete removal of the nitrogen, the gas was usually circulated for an additional three hours through a fresh tube of magnesium. The buret in which helium containing nitrogen from dissociation is collected is shown at 6; 15 is a mercury fall pump for circulating gases during the removal of nitrogen from helium. The gases during purification follow the path 20–29–15–18–13–19–20, Buret 6 being filled with mercury. During a decomposition, the path is 20–29–15–18–13–8–6. The movement of the gases in this step is caused by allowing mercury to run from Buret 6 into Reservoir 20. The flow of mercury, and thus indirectly of gas, is indicated by the drop across the capillary 27 as read at 25.

Analysis for nitrogen resulting from dissociation was made by absorbing the nitrogen by circulation through heated magnesium and later distilling ammonia from the magnesium nitride so formed into standard acid.

The alkaline sublimate from the heated cyanide was entirely condensed in the removable outlet tube of the Monel metal decomposition apparatus. Analysis for carbide was made by bubbling saturated sodium chloride solution up through this detached tube, drawing the acetylene liberated into a solution of silver nitrate and titrating the nitric acid liberated according to the equation:[7] $2AgNO_3 + C_2H_2 = Ag_2C_2 + 2HNO_3$. Cyanide was determined in the solution remaining after the evolution of acetylene and after thorough rinsing of the outlet tube. Total alkalinity was also determined by titration with standard acid. That part of the total alkalinity not due to sodium cyanide or carbide was considered as due to metallic sodium.

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[7] Yee and Krase, THIS JOURNAL, **46**, 1391 (1924).

Results

In the first series of experiments pure cyanide, previously fused, was placed directly in the charge chamber of the Monel metal apparatus (13 in Fig. 1). This chamber was provided with a ring of Monel at either end so that 2 or 3 g. of molten sodium cyanide could be retained as in a boat.

This method of procedure was, however, found to give erratic results. It appeared, for example, that the rate of decomposition was much greater at the start of the experiments than later. One possible explanation lay in assuming a diminishing catalytic action of the Monel metal on the dissociation and suggested the possibility that a catalyst might be required to maintain the decomposition rate throughout the experiment sufficiently high, so that the dissociation might approach equilibrium. Since iron was known[1] to catalyze the formation of sodium cyanide from sodium carbide and nitrogen, it appeared that it might likewise facilitate the dissociation. Accordingly, a series of experiments was next run, in which finely divided pure iron, prepared by reducing chemically pure magnetic oxide of iron with hydrogen, was mixed with the decomposing sodium cyanide.

Here again the results obtained were not reproducible. It was noted, in particular, that upon repeated heating of the same charge, the amount of decomposition was less than from a similar charge not previously heated. This seemed to indicate either (1) that any catalytic activity of iron on the thermal dissociation became impaired, or (2) that the iron was chemically decomposing sodium cyanide, as by the reaction, $NaCN + 3Fe = Fe_3C + Na + {}^1/_2N_2$, this action becoming less marked as the iron became more nearly saturated with iron carbide. It may be said that at least not all of the decomposition observed in these experiments was due to reaction with iron, since the amount of iron used was insufficient in a number of experiments to account for all of the cyanide decomposed, assuming all of the iron saturated with carbon in the form of iron carbide. Moreover, it was found that there was a measurable amount of dissociation even at 500° at which temperature iron carbide is unstable[8]; the observed decomposition at this temperature must hence be thermal in character. Then again, the dissociation indicated at higher temperatures after repeated use of the same charge was roughly the same as found in experiments to be described below in which iron was not included in the charge.

In view of the difficulty of definitely interpreting decomposition as purely thermal rather than chemical under conditions such that the cyanide could come in contact with metals, further experiments were all made in such a way that the cyanide came in contact with carbon only. For these experiments, a thin-walled graphite cylinder was fitted snugly inside the Monel metal cylinder. The outlet end of the graphite cylinder was a removable cap which permitted the introduction of the charge. Each end

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[8] Ruff and Goecke, *Z. angew. Chem.*, **24**, 1134 (1911).

of the closed cylinder was pierced by a 3mm. hole, the openings being made so small in order to minimize the diffusion of the dissociation products. The interior of this graphite-lined charge chamber was about 7 cm. × 1.3 cm.

The charge was prepared by fusing a mixture of about equal parts of sodium cyanide and carbon (petroleum coke). The function of the carbon was merely to provide a solid structure to hold the molten cyanide so as to facilitate the saturation of the gas with the decomposition products. The decomposition chamber was completely filled with small lumps of the material thus prepared.

Considerably better agreement was thus obtained (See Table I) between duplicate experiments although, as will be seen, the effect of changing conditions is not, in all cases, quantitatively such as would be expected. The correction of the apparent partial pressures as calculated directly from the analytical results is necessary because the sodium cyanide found in the outlet tube may be due not only to sodium cyanide distilled as such, but also to recombination in the cooler parts of the apparatus, of the dissociation products, sodium carbide and nitrogen. Corrections for this recombination have been made on the basis of the assumption that the gas leaving the decomposing sodium cyanide is saturated with sodium cyanide vapor, using published[9] data on the vapor pressure of sodium cyanide.

TABLE I

PARTIAL PRESSURES OVER SODIUM CYANIDE IN A HELIUM ATMOSPHERE; APPROXIMATE EQUILIBRIUM CONSTANTS

Sodium cyanide—Carbon charge in graphite-lined container

			Partial pressures, mm.							Equil. constants	
Expt.	Temp., °C.	Gas flow Cc./min.	Na	N_2		Na_2C_2		NaCN		$\frac{P^2_{Na}P_{N_2}}{P^2_{NaCN}}$	$\frac{P^2_{Na}}{P_{Na_2C_2}}$
				App.	Corr.	App.	Corr.	App.	Corr.		
1	600	3.15	...	22	...	...	..	..	..	..	..
2	1000	2.84	59	71	75	0.7	3.8	18.3	12	1800	916
3	1000	2.93	58	75	80	.6	5.7	22.2	12	1837	570
4	1000	2.90	77	56	59	.8	4.2	18.8	12	2425	1233
5	1000	1.70	88	60	74	.7	14.7	40.1	12	3990	530
6	1050	2.72	119	88	105	3.4	20.1	55	21	3350	590
7	1050	2.98	117	88	108	1.8	21.0	59	21	3360	656

It was to have been expected from Equations 5 and 6 that the partial pressure of sodium, P_{Na}, should have been given by the equation, $P_{Na} = 2(P_{N_2} - P_{Na_2C_2})$, if all of the dissociation products were carried out of the decomposition apparatus with the gas. It will be noticed, however, that the value of P_{Na} was in all cases considerably less than that calculated on this basis. In agreement with this, it was found that although the purity of the cyanide used was very high, there was at the end of the experiment from 4 to 7% of the total sodium held in some form other than cyanide,

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[9] Ingold, *J. Chem. Soc.*, **123**, 885 (1923).

possibly as metallic sodium absorbed on the carbon. Another portion of sodium was swept into the inlet tube and condensed there during the raising of the apparatus to the desired temperature.

Since it was found that the alkaline decomposition products could be quantitatively recovered from the outlet tube (that is, the amounts of non-cyanide alkali found in the apparatus corresponded to the nitrogen results) it appeared that it would be possible to study the decomposition in a nitrogen atmosphere, basing the calculations on the analysis of the sublimate in the outlet tube. A number of such experiments were, therefore, made with the results shown in Table II.

TABLE II

PARTIAL PRESSURES OVER SODIUM CYANIDE IN A NITROGEN ATMOSPHERE; APPROXIMATE EQUILIBIRUM CONSTANTS

Sodium cyanide—Carbon charge in graphite-lined container

			Partial pressure. Mm. of Hg							Equil. constants	
				N_2		Na_2C_2		NaCN			
Expt.	Temp., °C.	Gas flow Cc./min.	Na	App.	Corr.	App.	Corr.	App.	Corr.	$\frac{P^2_{Na}P_{N_2}}{P^2_{NaCN}}$	$\frac{P^2_{Na}}{P^2_{Na_2C_2}}$
1[a]	1050	3.02	56	682	...	0.9	..	21	..	5005	3500
2	1050	3.04	61	671	674	0.1	3.6	28	21	5960	1033
3	1100	2.95	51	655	663	1.7	9.7	53	21	1412	269
4	1100	2.92	66	634	646	1.4	13.7	60	35	2310	320
5	1100	3.01	67	625	640	2.7	18.0	66	35	2317	246
6	1100	2.81	67	621	637	3.9	20.6	68	35	2310	215
7[a]	1200	3.20	73	619	...	4.7	..	63	..	834	1138
8[a]	1220	3.13	92	562	...	3.2	..	104	..	435	2598
9[a]	1255	3.06	121	500	...	7.2	..	132	..	419	2028
10[a]	1255	6.49	100	587	...	3.0	..	78	..	971	3320
11	1255[b]	6.96	156	305	...	24.0	..	275	..	98	1013

[a] No correction (observed partial pressure of NaCN less than vapor pressure of NaCN) according to Ingold.

[b] Thermocouple junction out of place. Actual temperature appeared to be much higher, at least 1300°.

Discussion

The failure in these experiments to obtain more accurate and reproducible results may be attributed, in part at least, to the changing composition of both the liquid and gas phases during the experiments. Thus, starting with a charge of cyanide of high purity, supported on carbon, it is found, as was stated above, that an appreciable portion (4 to 7%) of the alkali in the charge at the end of the experiment was present in some other form than as cyanide. Assuming it to be adsorbed metallic sodium, it is evident that the concentration of sodium in the gas leaving the decomposition chamber would vary during a run since the portion of the liberated sodium adsorbed would change with the amount previously adsorbed on the carbon. Further variations in the gas phase in the experiments with a helium atmosphere were caused by decomposition of cyanide during the raising of the temperature before the helium flow was started. The manipulation at that stage of the experiment was such that the gas flow due to expansion was back through the inlet tube. The alkaline products of this preliminary decomposition were for the most part deposited in this inlet tube, but the nitrogen remained, of course, in the gas so that the first portion of gas passing into the decomposition chamber was not pure helium but the amount of contained nitrogen gradually decreased during the experiment. It appears then that the partial pressures calculated from the analytical results are only average values, whereas the calculations could be made only on the assumption that the partial pressures were constant.

The experiments show clearly that sodium cyanide is very appreciably dissociated either in an inert atmosphere or in nitrogen, at the temperatures employed and that, in fact, the vapor phase contains much more dissociated than undissociated sodium cyanide, at least at temperatures of 1000° to 1100°. If, as seems possible, the helium (or nitrogen) gas did not become saturated with decomposition products, then we can say that the dissociation of sodium cyanide was greater than indicated in these experiments.

So far as we can judge from these approximate values for the equilibrium constant $P^2_{\mathrm{Na}}P_{\mathrm{N_2}}/P^2_{\mathrm{NaCN}}$, as determined in the helium experiments, the dissociation increases with temperature as would be expected if the dissociation is an endothermic reaction. According to the experiments in nitrogen, however, at higher temperatures the dissociation appears to decrease with increasing temperature. This effect is consistent enough to have the appearance of reality, even though no satisfactory explanation for it can be offered at this time.

The effect of substituting nitrogen gas for helium in the decomposition experiments is qualitatively such as would be expected. At the same temperature, 1050°, the partial pressures of both sodium and sodium carbide are less in the nitrogen atmosphere. The amount of dissociation in nitrogen was, however, greater than was to be expected from the results of the helium experiments, as may be seen by a comparison of the value of $P^2_{\mathrm{Na}}P_{\mathrm{N_2}}/P^2_{\mathrm{NaCN}}$ in the two cases.

As to the erratic variations in the value of $P^2_{\mathrm{Na}}/P_{\mathrm{Na_2C_2}}$, it should be recalled that $P_{\mathrm{Na_2C_2}}$ is largely determined by the difference between the published[9] data on the vapor pressure of sodium cyanide and the apparent partial pressure of sodium cyanide in these experiments. Hence, the errors both in the determination of the vapor pressure of sodium cyanide and in the apparent partial pressure are multiplied in the value for $P_{\mathrm{Na_2C_2}}$ calculated. In any case, it appears that at the highest temperatures studied sodium carbide is still quite largely dissociated to sodium and carbon, since even after correcting for the recombination of sodium carbide with nitrogen, the concentration of sodium carbide is small as compared with that of metallic sodium. If we may judge from the experiments below 1100°, which give somewhat more consistent values for $P^2_{\mathrm{Na}}/P_{\mathrm{Na_2C_2}}$, it appears that the value of this constant decreases or, in other words, the stability of sodium carbide increases, with increasing temperature, as would be predicted from the endothermic character of sodium carbide.

Acknowledgment

The authors take pleasure in acknowledging their indebtedness to Dr. J. M. Braham for helpful criticisms and suggestions during the progress of this investigation.

Summary

1. A method is described for the preparation of sodium cyanide of high purity.

2. A method has been developed for the study of the thermal dissociation of sodium cyanide and the results are shown for the dissociation in an atmosphere of helium at 600°, 1000° and 1050° and in an atmosphere of nitrogen at 1050°, 1100°, 1200°, 1220° and 1255°.

3. Sodium carbide is shown to result from the dissociation as well as sodium, carbon and nitrogen.

4. The vapor above sodium cyanide is shown to consist largely of decomposition products. Thus, at 1050°, the partial pressures in millimeters of mercury in a helium atmosphere are approximately as follows: sodium 117; sodium carbide 21.0; nitrogen 108; sodium cyanide 21.

5. At all temperatures employed, sodium carbide is largely dissociated to sodium and carbon.

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[Contribution from the Wolcott Gibbs Memorial Laboratory, Harvard University]

THE ATOMIC WEIGHT OF URANIUM LEAD AND THE AGE OF AN ESPECIALLY ANCIENT URANINITE

By Theodore W. Richards and Lawrence P. Hall

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Measurement of geological time by radioactive disintegration appears at present to be the most trustworthy method for determining the age of minerals. In particular the lead-uranium ratio, as first suggested by Boltwood,[1] yields relative ages for geological strata which agree in general with those obtained from the helium-uranium ratio, and which can be reconciled, in part at least, with estimated ages depending upon purely geological observations.[2]

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[1] Boltwood, *Am. J. Sci.*, **23,** 77 (1907).

[2] (a) Barrell, *Bull. Geol. Soc. Am.*, **28,** 745 (1917). (b) Chamberlin, *Proc. Am Phil. Soc.*, **61,** 247 (1922).