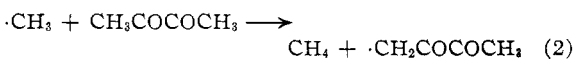


Fig. 1.—Acetone present during the decomposition of biacetyl at 436°. Initial pressure in the vicinity of 200 mm. (1) P_A is the pressure of acetone and P_0 , the initial pressure of biacetyl. (2) The % yield represents the pressure of acetone divided by the pressure of biacetyl decomposed.

added to 205 and 142 mm. biacetyl, the value of the pressure of acetone after 12.7 min. divided by the initial pressure of biacetyl averaged 2.5% in comparison with 2.5% from two experiments with biacetyl alone. From these results it does not appear that acetone is formed by secondary reactions involving ketene.

Comparison of the results of the previous investigation^{3b} with the present data shows that the amount of ketene is considerably larger than the amount of acetone in the initial stages of the decomposition. Under these conditions the ketene appears to result mainly from the reaction



followed by the decomposition of the $\cdot\text{CH}_2\text{COCOCH}_3$ radical to form ketene. The sum of the yields of ketene and acetone in the early portion of the reaction are closer to 100% than the yield of ketene alone.^{3b} Blacet and Bell² have reported energies of activation for reactions (1) and (2) and the ratio of the steric factors obtained from their data for the range 100–200°. From their values it can be calculated that reaction (2) should occur about three times as often as reaction (1) at 436°. The experimental results obtained in the thermal work confirm the greater importance of reaction (2); the ketene observed after 5.5 min. at 436° (67% yield) in the earlier work^{3b} is about five times the amount of acetone found in the present study. It is to be noted that the latter comparison does not provide an exact measure of the importance of reactions (1) and (2) since both ketene and acetone undergo subsequent reactions. The decreasing yield of acetone with time (curve 2, Fig. 1) can be explained by the loss of acetone in secondary reactions.¹² Moreover, the comparison will be affected if an appreciable fraction of the $\cdot\text{CH}_2\text{CO}$

COCH_3 radicals do not form ketene or if acetone or ketene results from reactions other than (1) or (2).

The mass spectrometric results and the ultra-violet data indicated the presence of small amounts of products other than those mentioned above, but the data did not provide an unequivocal identification of such products in the liquid mixture. Further investigation is needed to determine the identities and possible modes of formation of the minor products. By means of such information it may be possible to make a decision concerning the suggestion of Darwent¹³ that reaction (1) proceeds by the addition of the methyl radical to a carbonyl carbon atom of biacetyl.

(13) B. deB. Darwent, *Discs. Faraday Soc.*, 129, No. 14 (1953).

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Low Temperature Heat Capacity and Entropy at 298.16°K. of Analcite

By E. G. KING

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The mineral analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) has the chemical composition of jadeite ($\text{NaAlSi}_2\text{O}_6$), except for the water content. Structurally, of course, they are not similar. One very pertinent difference is the occurrence of aluminum as separate Al^{+++} ions in jadeite, whereas in analcite it occurs as AlO_4 -tetrahedra, replacing SiO_4 -tetrahedra in the silicate network. In this respect analcite is similar to albite ($\text{NaAlSi}_3\text{O}_8$) and nephelite ($\text{NaAlSi}_4\text{O}_{12}$). The geochemical relationship of analcite to albite, jadeite and nephelite (which has been under investigation elsewhere) required a knowledge of its entropy, thus furnishing the incentive for the present work. The entropies of albite, jadeite and nephelite have been reported previously.¹

Materials and Method.—The analcite was furnished by H. S. Joder, Jr., Geophysical Laboratory, Washington, D. C. Chemical analysis of a portion of the same sample was conducted by S. S. Goldich, Department of Geology, University of Minnesota, who obtained the following results: 13.44% sodium oxide, 22.36% alumina, 56.05% silica, 8.13% combined water, 0.10% potassium oxide, 0.02% magnesia, 0.01% titania, 0.03% ferric oxide, 0.01% adsorbed water, and less than 0.005% lime. These results are to be compared with the theoretical 14.08% sodium oxide, 23.15% alumina, 54.59% silica and 8.18% water. The material for the heat capacity measurements was dried 4 hours at 110° before use. For the purpose of correcting the heat capacity data, the sample was considered as containing 96.5% analcite, 3.3% silica and 0.2% water—an approximation based upon the analysis.

The heat capacity measurements were made with previously described apparatus.² The sample mass was 162.39 g.

Results

The measured heat capacity values, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, are in Table I. These values have been corrected for the major impurities (as indicated above) through use of heat capacity data for silica

(12) The data of J. A. Leermakers, *THIS JOURNAL*, **56**, 1899 (1934), and F. O. Rice, E. L. Rodowskas and W. R. Lewis, *ibid.*, **56**, 2497 (1934), indicate that although radicals may react with acetone molecules, a radical induced chain decomposition of acetone does not occur at 350–400°. Likewise the recent results of S. Kodama and Y. Takezaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **73**, 82 (1952), at 309° with methyl radicals do not show an induced chain decomposition.

(1) K. K. Kelley, S. S. Todd, R. L. Orr, E. G. King and K. R. Bonnickson, U. S. Bur. Mines Rept. of Investigation 4955 (1953).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

and ice listed by Kelley.³ The net correction ranged from 0.48 to 1.11%, depending upon the temperature. The thermal behavior of the substance was regular and an entirely normal type of heat capacity curve was obtained.

TABLE I
HEAT CAPACITY OF ANALCITE
(Mol. wt., 220.17)

$T, ^\circ\text{K.}$	$C_p,$ cal./deg. mole	$T, ^\circ\text{K.}$	$C_p,$ cal./deg. mole	$T, ^\circ\text{K.}$	$C_p,$ cal./deg. mole
53.42	10.83	114.59	25.15	216.33	41.72
57.77	11.93	124.57	27.14	225.93	43.02
62.43	13.03	135.81	29.25	237.75	44.51
67.38	14.51	145.87	31.05	245.73	45.43
72.24	15.69	156.03	32.78	256.58	46.58
77.05	16.84	166.26	34.44	266.28	47.61
79.93	17.55	175.98	35.92	275.91	48.66
83.52	18.39	185.95	37.38	286.32	49.40
94.43	20.86	195.98	38.79	296.21	49.98
105.44	23.21	206.45	40.21	298.16	(50.17)

The measured portion of the entropy, between 51 and 298.16°K., was obtained in the usual manner by Simpson-rule integration of the C_p against $\log T$ plot, as $S_{298.16}^\circ - S_{51}^\circ = 49.64$ cal./deg. mole. Extrapolation below 51°K. was accomplished by the adaptation of the method of Kelley, Parks and Huffman⁴ used previously¹ for treating heat capacity data of other alkali-aluminum silicates. The extrapolated portion of the entropy is $S_{51}^\circ = 6.39$ cal./deg. mole. The sum of the two increments gives $S_{298.16}^\circ = 56.0 \pm 0.6$ cal./deg. mole.

It is of interest to compare the entropy of analcite at 298.16°K. with those of albite, jadeite and nephelite, which are, respectively, 50.2 ± 0.4 , 31.9 ± 0.3 , and 29.7 ± 0.3 cal./deg. mole.¹ It was noted previously¹ that the entropy of jadeite is abnormally low in comparison with those of albite and nephelite, and this is to be associated with the higher atomic density of the jadeite and with the difference in mode of occurrence of the aluminum atoms in the crystals. The entropy of analcite is 24.1 units higher than that of jadeite and 16.0 units higher than the mean for albite and nephelite. Although both figures are larger than the entropy difference usually accompanying one mole of water difference in composition, they are entirely reasonable in view of the much looser structure of the analcite.

(3) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

(4) K. K. Kelley, G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

CONTRIBUTION FROM THE MINERALS
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The Rate of Decomposition of Ethane into Methyl Radicals¹

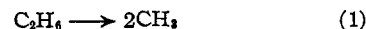
By C. H. LEIGH, M. SZWARC AND J. BIGEISEN

RECEIVED DECEMBER 6, 1954

The intention of this work is to determine the absolute rate of the dissociation of ethane into two

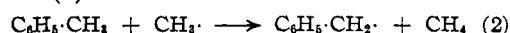
(1) Research carried out at the Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission.

methyl radicals. It is hoped that the continuation of this work will allow us to determine the activation energy of the dissociation process (1)



and from this the C-C bond dissociation energy in ethane. An accurate value for this heat might enable one to calculate the entropy of methyl radicals within one-half an entropy unit and thus determine which of the two models (planar or pyramidal) describes more correctly the structure of methyl radicals.

The investigation of the dissociation of ethane into methyl radicals was carried out in a flow apparatus, using the toluene carrier technique.² Methyl radicals produced in such a system are expected to react rapidly with toluene, present in a great excess, and to form methane according to equation (2)



Since the pyrolysis of toluene produces even a greater amount of methane³ than the pyrolysis of ethane, it is necessary to use ethane labeled by C^{14} in order to discriminate between the products of pyrolyses of toluene and of ethane. Consequently, the rate of reaction 1 was measured by the rate of formation of radioactive methane.

Experimental

The radioactive ethane was prepared from radioactive barium carbide containing 22% C^{14} . The hydrolysis of the latter compound produced labeled acetylene, and the hydrogenation of the acetylene led to the ethane. This high specific activity ethane was diluted by a factor of 10^5 with a non-active ethane, and then purified by scavenging it with non-active methane. The scavenging process was repeated until the ethane was found to contain no radioactive methane. The ethane was also scrubbed with an aqueous solution of cuprous ammonia chloride to remove unreacted acetylene.

The apparatus used in these studies was similar to one described previously.² The radioactive ethane is introduced into the toluene flow through a needle valve and a capillary, and its rate of flow was determined by the pressure drop across the capillary. The toluene vapor mixed with ethane flows through a silica reaction vessel heated electrically to the desired temperature. The gases emerging from the reaction vessel pass through one trap cooled by a carbon dioxide-acetone mixture and then through a second trap cooled by liquid nitrogen. The non-condensed products ($\text{H}_2 + \text{CH}_4$) are pumped by means of two mercury vapor pumps into storage flasks. A small trap, cooled by liquid nitrogen and introduced at the exit of the second mercury pump, prevents the presence of any C_2 hydrocarbons in the storage flasks.

This separation process is insufficient to yield a $\text{CH}_4 + \text{H}_2$ mixture free of radioactive contaminants, e.g., unreacted ethane and other C_2 's which may have been present as contaminants in the stock radioethane or formed in the pyrolysis. These were removed by a rigorous decontamination procedure, which was based on a repetitive dilution and extraction process.

The amount and the composition of the originally collected mixture of $\text{H}_2 + \text{CH}_4$ were determined by standard methods. Thereafter, a mixture of non-active ethane, ethylene and acetylene was admitted into the storage flasks. The ratio of scavenger gas to $\text{CH}_4\text{-H}_2$ mixture was about fifteen to one. The mixture of all these gases was circulated for a few minutes to provide adequate mixing, and thereafter they were circulated through a trap cooled by liquid nitrogen, until all the C_2 hydrocarbons were condensed out. The uncondensed $\text{H}_2 + \text{CH}_4$ was then returned to the storage

(2) M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949); *Proc. Roy. Soc. (London)*, **98A**, 267 (1949).

(3) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).