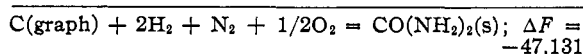
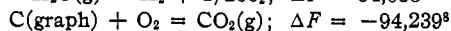
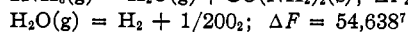
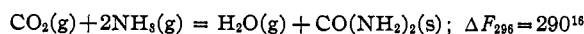


In view of our new combustion data and also of the availability of more reliable free energy data for water and carbon dioxide it is interesting to again compare the free energy of urea as calculated from equilibrium data and from third law data.

The calculation from the equilibrium data may be summed up as follows



This result is only 80 calories higher than the

(16) Lewis and Burrows, *THIS JOURNAL*, **34**, 1515 (1912).

(17) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 557.

third law value and is less than the uncertainty in the $T\Delta S$ term due to the uncertainty in the entropy of urea.

In conclusion we wish to thank Dr. E. L. Ellis for the purification of the compounds used in this investigation.

Summary

1. The isothermal heats of combustion of urea and guanidine carbonate have been determined at 25°.

2. The free energies of urea and guanidine carbonate have been calculated.

3. A comparison of the free energy of urea from equilibrium data and third law data has been made.

PASADENA, CALIF.

RECEIVED DECEMBER 28, 1939

[CONTRIBUTION FROM THE RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

The Crystal Structure of Sodium Formate, NaHCO_2 ¹

BY W. H. ZACHARIASEN

The present investigation was undertaken primarily to obtain accurate values for the structure of the formate group.

Crystals of sodium formate, NaHCO_2 , are reported² to have monoclinic-holohedral symmetry with crystallographic elements $a'_1:a'_2:a'_3 = 0.9196:1:1.6512$, $\alpha'_2 = 93^\circ 37'$. In this article another coordinate system, a_1, a_2, a_3 , will be used. The correlation between the two sets of axes is $a_1 = a'_1$, $a_2 = a'_2$, $a_3 = \frac{1}{2}(-a'_1 + a'_3)$, and one finds readily $a_1:a_2:a_3 = 0.9196:1:0.9700$, $\alpha_2 = 121^\circ 51'$.

The crystals studied were obtained by recrystallization from aqueous solutions. Most of the specimens obtained proved to be twinned with (001) as the twinning plane. The single crystals were elongated in the direction a_3 and showed the faces (010), (110) and (001). The compound is somewhat hygroscopic.

A great many oscillation photographs, using $\text{CuK}\alpha$ radiation, were prepared. The directions [001], [100], [101] and [010] served as rotation axes. The crystals were shaped into approximate cylinders along the various rotation axes so that corrections for absorption readily could be applied.

(1) Some of the results of this investigation were published in an abstract which appeared in *Phys. Rev.*, **53**, 917 (1938).

(2) P. Groth, "Chemische Krystallographie," Vol. III, Leipzig, 1901.

The structure determination was based upon the reflections in the equator layer lines for which the intensity was set proportional to

$$|F_H|^2 \frac{1 + \cos^2 2\theta}{\sin 2\theta} A$$

where A is the absorption factor.

The dimensions of the unit cell were found to be $a_1 = 6.19 \pm 0.01 \text{ \AA.}$, $a_2 = 6.72 \pm 0.01 \text{ \AA.}$, $a_3 = 6.49 \pm 0.01 \text{ \AA.}$, with $\alpha_2 = 121^\circ 42' \pm 10'$. The reported density of 1.91-1.93 gives four molecules of sodium formate in the unit cell. No reflections appear for which $H_1 + H_2$ is odd, so the translation lattice is base centered. Furthermore, reflections $H_1\text{OH}_3$ are absent if H_3 is odd, showing that the symmetry plane is a glide-plane rather than a reflection plane. On the assumption that the reported point group is correct, the space group becomes $C2_1/n(C_{2h}^6)$.

In order to obtain a reasonable structure for the formate group, carbon and hydrogen atoms must lie on the twofold rotation axes. A Patterson analysis of the reflections $H_1\text{OH}_3$ proved conclusively that the sodium atoms also occupy positions on the twofold axes while the eight oxygen atoms are in a set of general positions of the space group. The distribution of the atoms is accordingly as follows: 4 Na in $(\frac{1}{4}, u_1, \frac{1}{4})$, 4 H in

TABLE I
 OBSERVED AND CALCULATED STRUCTURE FACTORS

H ₁ OH ₁	F	F	H ₁ H ₂ O	F	F	H ₁ H ₂ H ₁	F	F	OH ₂ H ₂	F	F
002	-78	45	110	-2	9	11 $\bar{1}$	33	27	020	-59	35
20 $\bar{2}$	37	31	020	-59	35	020	-59	35	021	12	19
200	-8	14	200	-8	15	20 $\bar{2}$	37	31	002	-78	45
20 $\bar{4}$	-52	34	130	28	30	22 $\bar{2}$	-9	13	022	35	38
40 $\bar{2}$	-25	19	220	-10	15	13 $\bar{1}$	-41	21	040	-14	16
202	6	10	040	-14	16	31 $\bar{3}$	6	8	023	-23	25
004	29	20	310	-33	42	040	-14	16	041	11	15
40 $\bar{4}$	8	10	240	20	21	24 $\bar{2}$	-18	13	042	14	16
400	41	32	330	-9	9	40 $\bar{4}$	8	8	004	29	20
20 $\bar{6}$	43	23	150	-26	27	33 $\bar{3}$	4	4	024	-9	7
40 $\bar{6}$	-8	10	400	41	42	42 $\bar{4}$	6	6	043	6	7
204	-15	16	420	-18	19	15 $\bar{1}$	-1	0	060	17	13
60 $\bar{4}$	-41	22	060	17	14	060	17	10	061	-24	19
402	-40	25	350	18	20	51 $\bar{5}$	8	8	044	-12	9
60 $\bar{2}$	37	25	510	-10	11	35 $\bar{5}$	-30	16	025	26	17
006	-8	7	440	-10	8	44 $\bar{4}$	-14	9	062	-12	10
60 $\bar{6}$	30	15	260	1	0	26 $\bar{2}$	5	3	063	11	11
600	-21	14	530	21	17	53 $\bar{5}$	-6	5	006	-8	5
40 $\bar{8}$	14	9	170	-5	4	17 $\bar{7}$	15	9	045	-17	10
60 $\bar{8}$	-16	6	600	-21	12	60 $\bar{6}$	30	12	026	-1	0
			620	9	5	62 $\bar{6}$	-15	6	064	4	3
			460	8	4	46 $\bar{4}$	-2	0	080	-4	0
			370	-6	5	55 $\bar{5}$	-14	7	046	9	5
			080	-4	0	37 $\bar{3}$	28	11	081	6	4
			550	-18	8	080	-4	0	082	1	3
			280	-20	8	64 $\bar{6}$	-6	4			
						28 $\bar{2}$	11	3			
						71 $\bar{7}$	11	4			

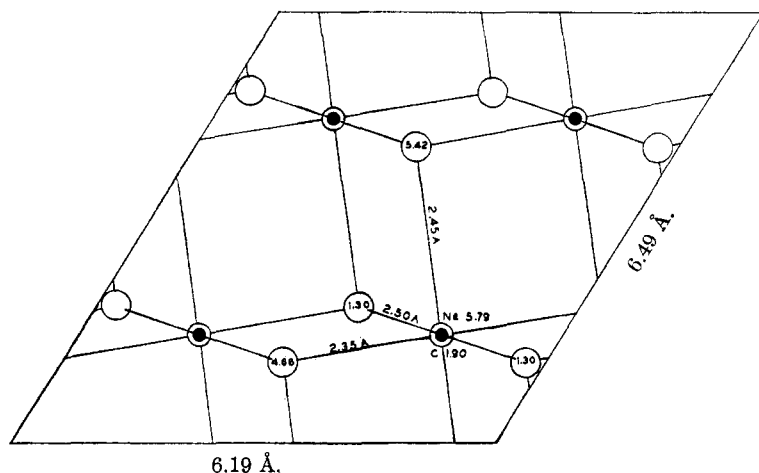


Fig. 1.—A projection of the structure on the (010) plane. Bonds between sodium and oxygen atoms are shown as connection lines. The length of the Na-O bonds and the heights of the atoms above the projection plane are indicated.

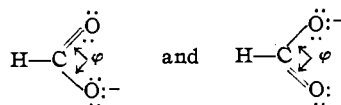
$\equiv (1/4, u_2, 1/4)$, 4 C in $\equiv (1/4, u_3, 1/4)$, 8 O in $\equiv (x_1, x_2, x_3)$.

Approximate values for the parameters u_1 , u_3 , x_1 , x_2 , x_3 were found without difficulty (since the hydrogen atoms play a negligible part in the scattering, the parameter u_2 cannot be determined

directly), while the accurate values were obtained from a series of Fourier projections. The results are: $u_1 = -0.139 \pm 0.001$; $u_3 = 0.283 \pm 0.002$; $x_1 = 0.043 \pm 0.002$; $x_2 = 0.194 \pm 0.002$; $x_3 = 0.185 \pm 0.002$. Setting $u_2 = 0.43$, one gets the reasonable value of 0.99 Å. for C-H separation in the formate group.

The agreement between observed and calculated structure factors is satisfactory, as shown in Table I. Figure 1 shows the projection of the crystal lattice on the (010) plane. As a consequence of the space group symmetry the two oxygen atoms are equivalent in the formate group, corresponding to

complete resonance between the two structures



The bond angle φ is 124° and the C-O distance is

1.27 Å. For the dimer of formic acid the values $\varphi = 125^\circ$ and C—O = 1.29 Å. were obtained from electron diffraction studies.³

Each sodium atom is linked to six oxygen atoms belonging to five different formate radicals. The sodium to oxygen distances are 2.35, 2.45 and 2.50 Å. with an average value of 2.44 Å., which is exactly equal to the distance predicted on the basis of ionic radii.⁴ The atoms are arranged in layers parallel to the (001) plane as shown in Fig. 1; the separation of the layers is 2.76 Å. Four of the six oxygen atoms bonded to a given sodium atom lie in the same layer and the other two in the two adjacent layers. The bonds between different layers are thus few in number (only one bond per 10.4 sq. Å.) and excellent cleavage parallel to (001) results.

An inspection of Fig. 1 will show that there is a pseudo twofold screw axis normal to the plane (001), *i. e.*, normal to the layers. As a consequence it becomes possible to obtain satisfactory binding between two consecutive layers when one layer is turned through 180° and displaced parallel to itself. This fact is directly responsible for the formation of twinned crystals so common in this compound. Figure 2 illustrates the structure of such a twinned crystal.

The optical properties of sodium formate crystals are not known; but it becomes possible to make some predictions. The optical anisotropy must be ascribed almost entirely to the presence of the formate groups. These are all parallel in the crystal and they are highly anisotropic. Thus the crystals must exhibit strong birefringence. The normal to the plane of the formate group is the direction of smallest polarizability, while the direction of greatest polarizability is in the plane of the group parallel to the connection line between the two oxygen atoms. It may accordingly be stated that (010) is the plane of the optical axes, and that the vibration direction corresponding to the smallest refractive index makes an angle of about 13° with a_3 in the obtuse angle α_2 .

(3) L. Pauling and L. O. Brockway, *Proc. Natl. Acad. Sci. U. S.*, **20**, 336 (1934).

(4) W. H. Zachariasen, *Z. Krist.*, **80**, 137 (1931).

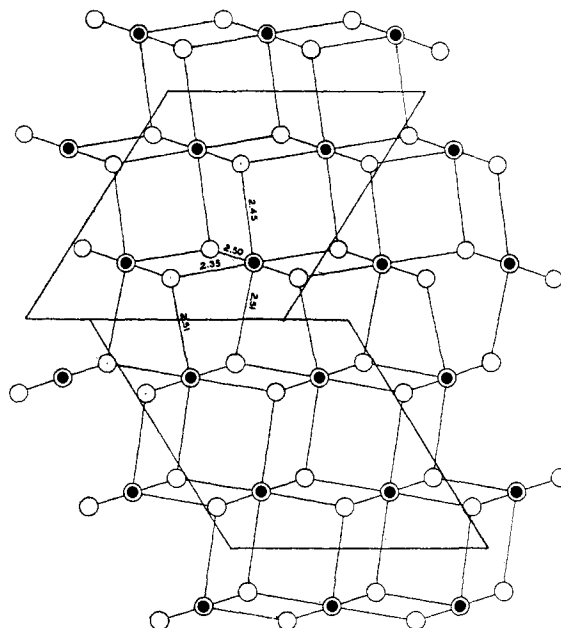


Fig. 2.—This illustrates the explanation of the observed twinning.

Summary

Crystals of sodium formate are monoclinic with four molecules of sodium formate per unit cell. The lattice dimensions are: $a_1 = 6.19 \pm 0.01$ Å., $a_2 = 6.72 \pm 0.01$ Å., $a_3 = 6.49 \pm 0.01$ Å., $\alpha_2 = 121^\circ 42' \pm 10'$. The space group is $C2/c(C_{2h}^2)$. Sodium, hydrogen and carbon atoms are on two-fold rotation axes, oxygen atoms in general positions. The parameter values are:

	x_1	x_2	x_3
Na	1/4	-0.139 ± 0.001	1/4
C	1/4	$.283 \pm .002$	1/4
H	1/4	.43	1/4
O	0.043 ± 0.002	$.194 \pm .002$	0.185 ± 0.002

There is complete resonance between the two C—O bonds of the formate group. The C—O distance is 1.27 Å. and the bond angle is 124° . Sodium has six oxygen neighbors at an average distance of 2.44 Å.

CHICAGO, ILLINOIS

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