Crystalline $Cu(OH)NH_4CrO_4$ precipitated in the first step of the preparation of "copper–chromium oxide" catalyst, is decomposed at relatively low temperatures to produce an equimolar mixture of cupric oxide and cupric chromite, the normal catalyst. Very high temperature ignition of the catalyst causes their complete combination to form cuprous chromite. Microscopic and X-ray data indicate the latter substance to crystallize in the hexagonal system with two $Cu_2Cr_2O_4$ per unit cell, a_0 = 2.975 Å., c_0 = 17.096 Å.

Normal "copper–chromium oxide" catalysts used in typical low temperature hydrogenations show partial or complete reduction to metallic copper and cuprous chromite. Ordinary reclamation processes succeed only in removing organic matter and re-oxidizing the copper but complete return to the chemical composition of the original catalyst can be accomplished by a relatively long, low temperature "annealing" treatment.

RECEIVED JUNE 16, 1948

[CONTRIBUTION FROM INSTITUTT FOR UORGANISK KJEMI, NORGES TEKNISKE HÖGSKOLE]

The Equilibrium $CaCO_{3(melt)} = CaO_{(s)} + CO_2$. The Activity Coefficients of Calcium Carbonate in Alkali Carbonate Melts

BY H. FLOOD, T. FÖRLAND AND B. ROALD

Experimental

The equilibrium diagram of the system calcium carbonate–sodium carbonate–carbon dioxide (p_{CO_2} = 1 atm.) has been examined by P. Niggli,[1] and later by W. Eitel.[2] A sketch of the diagram is shown in Fig. 1a. Only the right-hand side of the diagram is of interest in connection with the questions to be treated here. At the composition ratio 1:1, a compound ($CaCO_3 \cdot Na_2CO_3$) appears which is decomposed at temperatures above 817°. Solid calcium carbonate does not dissolve appreciable amounts of sodium carbonate. The solubility of calcium carbonate in the melt increases with the temperature (compare the curve DA). At about 900° the carbon dioxide tension of solid calcium carbonate exceeds 1 atm. Above this temperature only calcium oxide, not calcium carbonate, can exist in equilibrium with the melt. The composition of the melt in equilibrium with calcium oxide at 1 atm. carbon dioxide pressure is given by the curve AB. The curve AB has been only roughly estimated in the previous publications. Thus in the diagram of W. Eitel it is drawn with the curvature the wrong way.

By assuming calcium oxide insoluble[3] in the melt, however, the curve AB can be determined by a simple gravimetric procedure.

Starting with a melt, for instance, of composition and temperature corresponding to the point N_1, T_1 (compare Fig. 1b), and raising the temperature to T_2, calcium oxide will be precipitated and carbon dioxide expelled until the composition of the melt corresponds to N_2. This composition is given by the amount of carbon dioxide expelled, which is determined by weighing. By further raising of the temperature to T_3 another composition corresponding to N_3 will be found after adjustment of the equilibrium, etc. In this way the curve AB may be determined.

The experiments were carried out in an apparatus previously used in the investigation on the reactions of polyacids with alkali carbonate[4] (compare also ref. 1). As precipitated calcium oxide proved to re-dissolve very slowly in the melts, the experiments were always carried out at rising temperatures.

The platinum crucible with the weighed charge was placed in the heating zone of the furnace and kept there at a constant temperature about twenty minutes. Then it was quickly as possible removed, cooled in a desiccator and weighed (in a weighing bottle).

In addition to the system mentioned, the system with potassium carbonate was examined. Also a few experiments with lithium carbonate were carried out. The results are given in Table I and a graphical representation is shown in Fig. 2. The potassium and sodium systems give results with smaller limits of error than the lithium system. It seems that basic lithium melts may cause an attack on the platinum crucible.

TABLE I

Experiment	Temperature, °C.	Mol. 10^{-3} CaO precip.-CO_2 expelled	$CaCO_3$	K_2CO_3	N_{CaCO_3}
		A. K_2CO_3–$CaCO_3$			
I	20	0	11.10	5.62	(66.4)
	971	3.93	7.12	5.62	55.9
	1078	7.88	3.22	5.62	36.4
II	20	0	6.18	3.47	(64.0)
	1008	2.93	3.25	3.47	47.9
	1063	3.91	2.27	3.47	39.5
	1105	4.43	1.75	3.47	33.5
		B. Na_2CO_3–$CaCO_3$			
I	20	0	9.18	9.04	(50.4)
	964	1.60	7.58	9.04	45.6
	1044	5.67	3.51	9.04	28.0
II	20	0	9.68	8.47	(53.3)
	1005	5.01	4.67	8.47	35.5
	1097	7.52	2.16	8.47	20.3
		C. Li_2CO_3–$CaCO_3$			
I	20	0	7.00	12.04	(36.8)
	971	1.35	5.65	12.04	32.0
	1034	4.23	2.77	12.04	18.7
II	20	0	8.36	13.57	(38.1)
	1018	4.19	4.17	13.57	23.5

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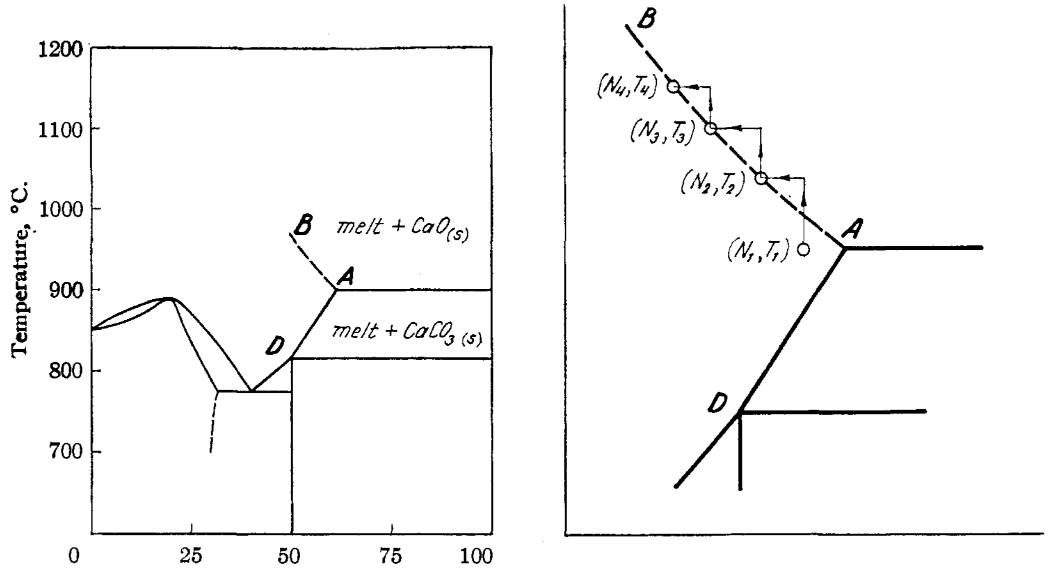
(1) P. Niggli, *Z. anorg. Chem.*, **98**, 241 (1916).

(2) W. Eitel, *Tschermak's Min. Petr. Mitt.*, **38**, 1 (1925).

(3) A correction can be made for the solubility of calcium oxide in the melt by examining the amount of expelled carbon dioxide at temperatures and compositions just below the curve AB. The experiments indicated that the correction was negligible.

(4) H. Flood, T. Förland and B. Roald, unpublished.



(a) N_{CaCO_3}. (b) N_{CaCO_3}.

Figs. 1a and b.—The equilibrium diagram of the system calcium carbonate–sodium carbonate when $p_{CO_2} = 1$ atm.

Discussion

The data given in Table I and Fig. 2 can be used for a discussion of the deviations of the melts from ideal solutions. We denote by p'_{CO_2} the carbon dioxide pressure above a molten mixture of calcium carbonate and alkali carbonate in presence of solid calcium oxide according to the equilibrium

$$CaCO_3(m) = CaO(s) + CO_2(g)$$

On the other hand, the carbon dioxide pressure p_{CO_2} according to the equilibrium

$$CaCO_3(s) = CaO(s) + CO_2(g)$$

is fairly well investigated. K. K. Kelley and C. T. Anderson[5] give the following formula for $p_{CO_2} = K$

$$RT \ln K = 42.500 + 1.52T \log T + 2.155.10^{-3}T^2 - 0.0205.10^5T^{-1} - 34.58T$$

In the following we denote the activities of calcium carbonate in the solid state by a_s, in the liquid state by a_l and in molten mixtures by a_m. Then

$$a_m/a_s = p'_{CO_2}/K \qquad (1)$$

and when the carbon dioxide pressure above the melt is 1 atm.

$$a_m/a_s = 1/K \qquad (2)$$

Introducing a_l in numerator and denominator we have

$$\frac{a_m}{a_l}\frac{a_l}{a_s} = \frac{1}{K} \qquad (3)$$

and

$$RT \ln \frac{a_m}{a_l} + RT \ln \frac{a_l}{a_s} + RT \ln K = 0$$

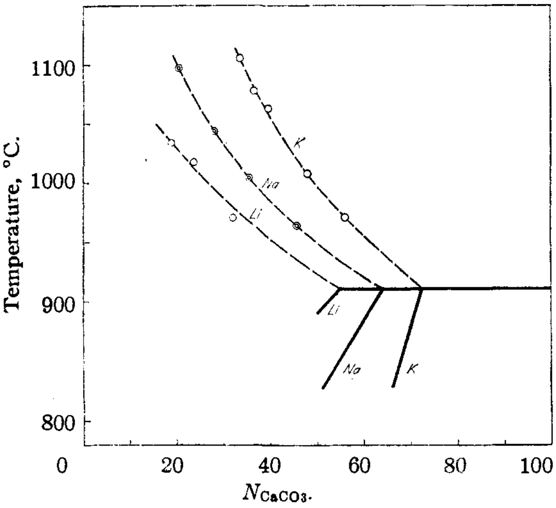


Fig. 2.—The equilibrium diagrams of the systems calcium carbonate–potassium carbonate, calcium carbonate–sodium carbonate and calcium carbonate–lithium carbonate when $p_{CO_2} = 1$ atm.

The term $RT \ln \frac{a_l}{a_s}$ is the change in free energy for the process

$$CaCO_3(s) \longrightarrow CaCO_{3(\text{pure liquid})}$$

at the same temperature. If we denote the heat absorbed in the melting process by ΔH, and T_0 is the melting point for calcium carbonate, we have

$$RT \ln \frac{a_m}{a_l} + RT \ln K + \Delta H \left(1 - \frac{T}{T_0}\right) = 0 \qquad (4)$$

neglecting the variation of ΔH with the temperature.

Now we will choose $CaCO_3$ (pure liquid) as stand-

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[5] K. Kelley and C. T. Anderson, Bull. 384, Bureau of Mines (1935).

ard state. Introducing f_1 for the activity coefficient and N_1 for the mole fraction of calcium carbonate in the molten mixture, we get $a_l = 1$ and

$$RT \ln f_1 = -RT \ln N_1 - RT \ln K - \Delta H\left(1 - \frac{T}{T_0}\right) \quad (5)$$

This equation contains two unknown f_1 and ΔH. T_0 has been found by Smyth and Adams to be 1340°.[6] J. H. Hildebrand and E. J. Salstrom[7] have investigated mixtures of silver bromide–alkali bromide by aid of e. m. f. measurements. They find that the melts behave as "regular solutions"; this means that the entropy of mixing is the same as for an ideal mixture. This is expressed by the equation

$$RT \ln f_{\text{AgBr}} = bN^2_{\text{Alk. Br.}}$$

where f is the activity coefficient, N, the mole fraction and b a constant individual for each alkali metal. In the rubidium and potassium systems b is positive, but in the sodium and lithium systems b is negative. Hildebrand and Salstrom connect this with the fact that the ionic radii of the two former are larger than the radii of the two latter alkali metal ions.

We will now examine if similar simple rules are valid in the molten carbonate mixtures. From eqn. 5 we have

$$\frac{RT \ln N_1K}{1 - \frac{T}{T_0}} + \frac{RT \ln f_1}{1 - \frac{T}{T_0}} + \Delta H = 0$$

If the melt behaves as a "regular solution," we should get a straight line by plotting $-RT \ln N_1K/1 - (T/T_0)$ against $N_2^2/1 - (T/T_0)$ (N_2 is the mole fraction of alkali carbonate). Compare Fig. 3. It appears from the diagram that the experimental values, at least in the case of potassium and the sodium systems, are well represented by straight lines, with a mutual intercept for $N_2^2 = 0$, giving

$$\Delta H = 3.400 \pm 600 \text{ cal.}$$

We may therefore write

$$RT \ln f_1 = bN_2^2$$

where b is an individual constant for each alkali carbonate system. The melts in fact seem to behave as regular solutions.

(The principal error in this calculation is caused by inaccuracies in the estimation of the temperature. The temperature in the heating zone was constant during the adjustment of the equilibrium with an accuracy of ±1°. This leads to an uncertainty in the computation of K corresponding to $d \log K/dT = 0.01$. At 1000° this corresponds to ±70 cal.)

The slopes of the straight lines give values of b. The b-values of Hildebrand and Salstrom for the bromide systems, which also are given in Table II, show that the deviations from ideal solution are distinctly smaller in the bromide mixtures where the mixing cations are of equal electric charge than in the carbonate mixtures where the electric charges are different.

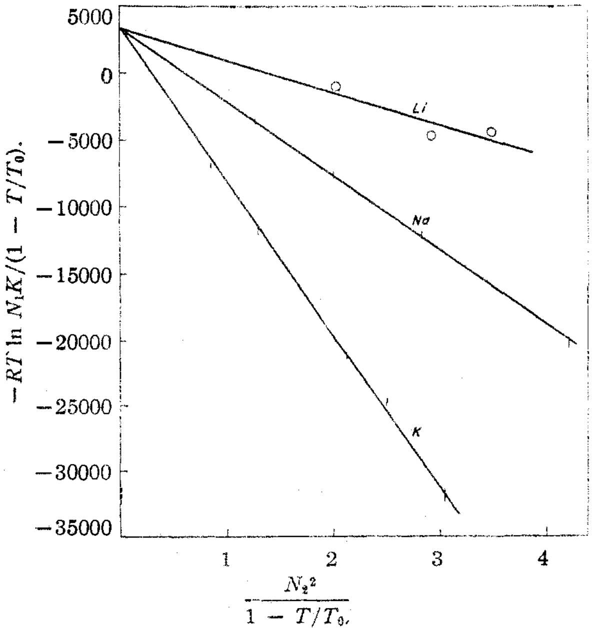

Fig. 3.

Table II

	$CaCO_3 + (Alk.)_2CO_3$, cal.	AgBr + Alk. Br, cal.
K	−11500	−1480
Na	− 5500	+1050
Li	− 2400	+1880

Having found the values of ΔH and b, we are able to give the formula for the calculation of the curve AB (Fig. 1) at any carbon dioxide pressure. For a carbon dioxide pressure (p'_{CO_2}) above the melt different from 1 atm., eqn. 3 will have the form

$$\frac{a_m}{a_1} \cdot \frac{a_1}{a_s} = \frac{p'_{CO_2}}{K}$$

and eqn. 5 will have the form

$$RT \ln p'_{CO_2} = RT \ln K + RT \ln N_1 + RT \ln f_1 + \Delta H\left(1 - \frac{T}{T_0}\right)$$

substituting for $RT \ln f_1$ we get

$$RT \ln p'_{CO_2} = RT \ln K + RT \ln N_1 + bN_2^2 + \Delta H\left(1 - \frac{T}{T_0}\right)$$

which is the equation for the curve AB at any carbon dioxide pressure. The limit $p'_{CO_2} = K$ corresponds to the co-existence of $CaCO_3$(s), (CaO(s)) and $CaCO_3$–$(Alk)_2CO_3$ melt. This gives the equation

$$RT \ln N_1 + b(1 - N_1)^2 + \Delta H(1 - T/T_0) = 0$$

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(6) F. H. Smyth and L. H. Adams, *ibid.*, **45**, 1167 (1923).

(7) J. H. Hildebrand and E. J. Salstrom, This Journal, **54**, 4257 (1932).

(This result may also be derived from the Clausius–Clapeyron formula considering the melt as a regular solution.) The calculated curve checks only fairly with W. Eitel's measurements of the same phase diagram. However, there is also quite a difference in decomposition temperature for $CaCO_3$(s) at $p_{CO_2} = 1$ atm. given by W. Eitel (900°) and given by K. Kelley (884°). Our calculations are based upon K. Kelley's data.

The authors express their thanks to Det Videnskapelige Forskningsfond av 1919 and Norges tekniske høgskoles Fond for grants.

Summary

1. By means of a simple gravimetric procedure the composition of calcium carbonate–alkali carbonate melts in equilibrium with solid calcium oxide at a carbon dioxide pressure of 1 atm. has been determined.

2. On the basis of these results calculation of the activity coefficient of calcium carbonate in the melt is discussed. It follows that the carbonate mixtures behave as regular solutions.

3. The heat of fusion of calcium carbonate is calculated to 3400 cal.

TRONDHEIM, NORWAY RECEIVED AUGUST 4, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Reactions of the Silver Salts of Carboxylic Acids with Iodine in the Presence of Some Tertiary Amines

BY RALPH A. ZINGARO, JUDSON E. GOODRICH, JACOB KLEINBERG AND CALVIN A. VANDERWERF

Recent reports[1,2] that monopyridine iodine (I) *p*-nitrobenzoate is toxic *in vitro* to certain fungi have reawakened interest in base stabilized iodine salts of organic acids.[3]

The purpose of the present work was the preparation of a series of positive iodine salts of organic acids, using pyridine or α- or β-picoline as the coördinating agents, with the intent of finding new compounds which may be effective against bacteria and fungi. Thirty-one of these salts have been prepared and pertinent data concerning them are collected in the tables. The percentage yields are based on the silver salt used and not on the amount of iodine which reacted. In those cases where pyridine was the coördinating agent, the aromatic acids used were selected in such a way as to permit comparisons of the effects on the yield of desired product of various substituents at different positions on the aromatic acid ring.

In many of the reactions where the yield of iodine salt was low, recovery of appreciable free acid was realized even under rigorously anhydrous conditions. For example, in the attempt to prepare α-picoline iodine (I) *p*-bromobenzoate, *p*-bromobenzoic acid was recovered in over 70% yield. This may mean that the formation of the iodine compound and the formation of the free acid are competing reactions.

TABLE I

DERIVATIVES OF α- AND β-PICOLINE IODINE (I)

	α				β			
	M. p., °C. (uncor.)	Yield, %	Iodine, %		M. p., °C.	Yield, %	Iodine, %	
			Calcd.	Found			Calcd.	Found
Benzoate	122–124dec.	9	37.2	37.1 36.9	123–126dec.	24	37.2	37.1 37.2
o-Nitrobenzoate	116–119dec.	14	32.9	32.7 32.6	88–91	36	32.9	33.0 33.0
m-Nitrobenzoate	139–143	53	32.9	33.0 32.8	134–137dec.	32	32.9	32.5 32.5
p-Nitrobenzoate	163–165dec.	14	32.9	32.9 32.9	188–191dec.	52	32.9	33.0 32.8
3,5-Dinitrobenzoate	159–162dec.	64	29.4	29.3 29.2	164–167dec.	32	29.4	29.1 29.1
p-Chlorobenzoate	113–116dec.	21	33.8	34.2 34.0	129–132dec.	17	33.8	33.6 33.5
p-Bromobenzoate	......	..	..	.. ..	127–129dec.	14	30.2	30.3 30.2
p-Iodobenzoate	118–121dec.	30	27.2	27.2 26.9	116–120dec.	50	27.2	27.0 27.5

Experimental

Preparation of Reagents.—Since positive iodine compounds decompose in the presence of water, anhydrous conditions must be maintained throughout in their preparation. The chloroform and Skellysolve A were dried over calcium chloride and distilled; the commercial absolute ether was dried over sodium and distilled. The pyridine and α- and β-picoline were dried over sodium hydroxide pellets for two weeks and distilled, the distillates boiling at 114.5 and 128.1° at 740 mm. and 141.7° at 735 mm., respectively, being collected.

Preparation of Silver Salts of the Acids.—The organic acid was dissolved in hot alcohol and a hot aqueous solu-

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(1) Kleinberg, Novak and Gerberg, *Proc. Soc. Exp. Biol. Med.*, **58**, 238 (1945).

(2) Kleinberg and Meyer, *Science*, **104**, 398 (1946).

(3) The following references describe the intermediate complex compounds formed by the action of iodine on the silver salts of organic acids, the various types of decomposition of these substances, mechanisms proposed for these reactions, and the use of pyridine as a coördinating base in the formation of positive iodine salts of organic acids: (a) Simonini, *Monatsh.*, **14**, 81 (1893); (b) Wieland and Fischer, *Ann.*, **446**, 49 (1925); (c) Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934); (d) Prévost, *Compt. rend.*, **196**, 1129 (1933); (e) Birckenbach and Meisenheimer, *Ber.*, **69B**, 723 (1936); (f) Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einwertigen Iods," Verlag von S. Hirzel, Leipzig, 1932.