84. *The System* $CaCO_3$–$CaSO_4$–H_2O *at* 159° *to* 252°, *and the Effect of Additions of Sodium Salts.*

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A NORMAL boiler-feed water has in solution small quantities of sparingly soluble salts, in particular those of calcium. The concentration of the solution accompanying the production of steam is usually carried so far that solid salts are precipitated. If the salts are less soluble at high than at low temperatures, the rise in temperature alone may be sufficient to cause precipitation. The commonly occurring precipitates are calcium sulphate, which usually appears as a hard adherent scale on the heating surfaces, and calcium carbonate, which normally forms a sludge.

A thickening and adherent scale causes uneconomic working, and many attempts have been made to discover why some substances adhere to the tubes while others do not (for bibliography, see Partridge, " Formation and Properties of Boiler Scale," Univ. of Michigan Eng. Res. Bulletin No. 15, 1930). Since the mechanism of scale formation is not fully understood, the deposition of calcium sulphate as a sludge cannot be ensured and it is more profitable to consider methods of preventing its appearance as any kind of solid phase. The theory of the first successful method was investigated by Hall (*J. Ind. Eng. Chem.*, 1925, **17**, 283), who proposed to precipitate the calcium solely as carbonate sludge, by adjusting the relative amounts of carbonate and sulphate in the water. Theoretically, only calcium carbonate can be precipitated if the ratio of carbonate to sulphate exceeds the ratio of the solubility products of the two salts for the working temperature. It is quite clear that in practice only calcium carbonate will be precipitated if the CO_3/SO_4 ratio exceeds a certain magnitude, but this magnitude will only equal the ratio of the solubility products

if the solution behaves as an ideal one.   In the absence of adequate solubility data, Hall estimated the critical CO$_3$/SO$_4$ ratios from the ratio of the solubility products at the various temperatures, that of the sulphate being calculated from the solubility of anhydrite at boiler temperatures, and that of the carbonate from an extrapolation of Kendall's measurements (*Phil. Mag.*, 1912, **23**, 958) of the solubility of calcite between 20° and 100°.   The ratios thus obtained increased rapidly with rising temperature, and led to a carbonate content, at pressures above 250 lb./sq. inch, which would be so high as to cause risk of caustic embrittlement because of the production of a relatively high caustic alkalinity by decomposition of sodium carbonate.

It was thought, however, that lower ratios might suffice in practice, and work on the actual CO$_3$/SO$_4$ ratios in solutions of compositions similar to those of boiler waters was undertaken.   The work has fallen into two divisions : The determination of the CO$_3$/SO$_4$ ratios for co-existence of the carbonate and sulphate (as calcite and anhydrite) in the system CaCO$_3$-CaSO$_4$-H$_2$O between 159° and 255° (1) without added compounds, and (2) with addition of sodium sulphate, chloride, or hydroxide.

EXPERIMENTAL.

A 2-litre Bergius rotary converter made of Firth's " H.R. Crown Max," designed for work at temperatures up to 400° and pressures up to 600 atm., was adapted to solubility work.   The

Fig. 1.
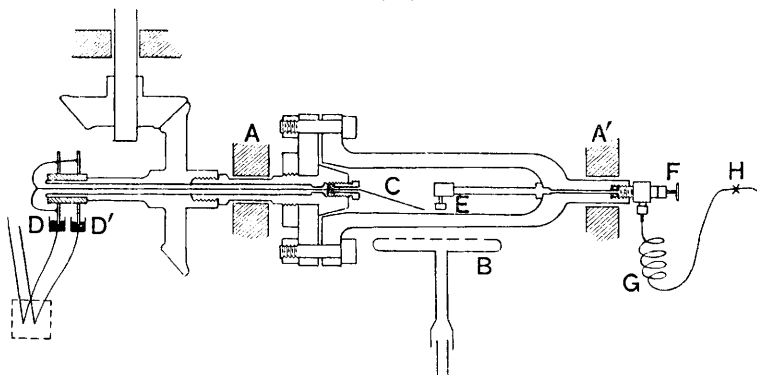
arrangement is shown in Fig. 1.   The converter was held in the two bearings, A,A′ and could be rotated about this axis at a speed of 14 r.p.m.   It was covered with a cowl, and heated by the gas burner B.   The temperature was measured with a calibrated chromel–alumel couple within the sheath C.   This sheath, made of stainless steel, was bent to within $\frac{1}{4}''$ of the inner bomb wall. The leads from the couple were connected to two insulated copper discs which dipped into the mercury troughs D,D′, from which chromel and alumel wires ran to cold junctions with copper. The wiring was arranged so that the *E.M.F.* could be measured with either a potentiometer or a recording instrument.   By opening the valve F, samples for analysis could be withdrawn from the bomb through the filter E, which was fixed near the thermocouple top, about $\frac{1}{4}''$ from the bomb wall.   Satisfactory filters were made by copper- or silver-plating small pieces of fine phosphor-bronze gauze until the interstices were small enough to act efficiently as filters (Manning, J., 1926, 1127).

A gas supply from a main served by a booster through a constant-pressure device was available, and there was no difficulty in regulating the supply with a fine-adjustment valve so that temperatures constant to $\pm$ 1·5° could be maintained.

In order to prevent evaporation, it was necessary to cool the sample before releasing it to atmospheric pressure.   A cooling coil G, of copper capillary, was provided, fitted with a valve H. When a sample was to be taken, the rotation of the converter was stopped, and the cooling coil attached to the valve F.   The coil was cooled with water and the valve opened.   Rate of flow was governed by the valve H.   As would be expected from the retrograde solubilities of calcium carbonate and calcium sulphate at high temperatures, cooling threw out no solid from solution. During the time taken for sampling, the temperature of the bomb as shown by the thermocouple was controlled in the normal way.   Halting the stirring during sampling had no disturbing effect

on the equalisation of temperature throughout the bomb, for when rotation was recommenced no change in the thermocouple E.M.F. could be detected.

The bomb was charged in the following way. Equal weights of calcium carbonate (Hopkin and Williams; Ca, 39·45; CO_3, 59·93; SiO_2, 0·0019; Fe_2O_3, 0·0013% ; Ba not detected) and anhydrous calcium sulphate (B.D.H.; Ca, 29·60; SO_4, 70·90%) were placed in the dry clean bomb, which was then closed, placed in position, and heated to about 80°. The weights of solid taken depended on the composition of solution added later, and varied between 1 g. of each for the system $CaCO_3$–$CaSO_4$–H_2O to 3 g. of each for solutions containing the higher concentrations of sodium sulphate or hydroxide. The bomb was evacuated through the valve F, and about 1300—1500 c.c. of distilled water or of a solution containing sodium salts in known concentration, previously boiled to remove dissolved gas and then cooled to 80°, were sucked in. By following this method, the risk of hydration of calcium sulphate was avoided. After closing the valve F, rotation of the bomb was started, and the temperature raised to the proper value. The stirring at constant temperature was continued for at least 24 hours. During the last 4 or 5 hours, particular care was taken with the hand control to keep the temperature steady to $\pm$ 1·5°. The first 100 c.c. of sample from the bomb were rejected, the following 1000 c.c. were run through a filter-paper into a calibrated flask and kept for analysis. A very slight discoloration of the filter-paper showed that some substance had been retained on it, but this deposit gave no sulphate reaction and no titration with acid, and its weight was negligible. The filtered sample was colourless and clear. The deposit probably came from the filter plates; it was more noticeable with copper than with silver filters. On opening the bomb soon after sampling, both calcite and anhydrite were always found as solid phases as pure white powders.

During the sampling period, measurements of the thermocouple E.M.F. were made frequently with the potentiometer. After sampling, the converter was again rotated, and the temperature measured to make sure that there had been no disturbance of the temperature equilibrium.

The sodium sulphate and sodium chloride solutions were made up from A.R. materials; the sodium hydroxide solutions were prepared by diluting standard solution of negligible carbonate content with carbon dioxide-free water.

Analysis.—(a) *System* $CaCO_3$–$CaSO_4$–H_2O. The samples were evaporated to dryness without boiling, on a hot-plate in weighed crystallising dishes of 8-cm. diameter, and the total solid determined by weighing the deposit after the dish had been heated to 150° for some hours, whereby the calcium sulphate was left as hemihydrate. It had been shown that these dishes exhibited no alkaline residue or change in weight after the evaporation in them of 1 l. of distilled water, so it was possible to determine the calcium carbonate content of a sample by titrating the residue with N/10-hydrochloric acid, using methyl-orange as indicator.* The residue was then digested with a small quantity of fairly concentrated hydrochloric acid until the calcium sulphate had dissolved, and the solution was then made up to 250 c.c. in a calibrated flask. Portions of this solution were taken for sulphate and calcium determinations, the former gravimetrically as barium sulphate, and the latter as oxalate, which was either converted into oxide and weighed, or determined by the permanganate method.

(b) *System* $CaCO_3$–$CaSO_4$–H_2O *with added salts.* Except for the equilibria reached from solutions containing added sodium hydroxide, the analytical methods were the same as those above, but silver dishes were used for the evaporation. In addition, determinations of the caustic alkalinity produced by hydrolysis were made on separate samples. The solutions containing added sodium hydroxide were analysed without evaporation to dryness, by determining the carbonate by the carbon dioxide evolution method and subtracting the equivalent carbonate from the total alkalinity to get the hydroxide content.

The samples were collected and their volumes measured at room temperature. Since the concentrations of dissolved substances are low, they can be expressed for all practical purposes as either g. per litre at room temperature or g. per 1000 g. of water.

Results.—The results are in Tables I—IV. Table I gives the equilibria in the system $CaCO_3$–$CaSO_4$–H_2O. The solubility of calcium carbonate is known to depend on the partial pressure of carbon dioxide over the solution. In the present case a closed vessel was used containing solution made up from carbon dioxide-free water and this pressure was presumably the very low pressure reached by the system itself through the decomposition pressure of calcium carbonate.

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* The caustic alkalinity formed in the solution at 250° was measured. This proved to be very small, being only 7% of the carbonate content. Since this 7% at 250° is likely to be the maximum for the range studied and is no greater than the over-all experimental error, no account has been taken of it.

TABLE I.

Composition of Solutions in Equilibrium with Solid CaSO$_4$ *(Anhydrite) and* CaCO$_3$ *(Calcite) in the System* CaCO$_3$–CaSO$_4$–H$_2$O.

Temp.	Total solid (CaSO$_4$,½H$_2$O + CaCO$_3$), g./1000 g. H$_2$O. By evaptn.	By analysis.	G./1000 g. H$_2$O. Ca.	SO$_4$.	CO$_3$.	Temp.	Total solid (CaSO$_4$,½H$_2$O + CaCO$_3$), g./1000 g. H$_2$O. By evaptn.	By analysis.	G./1000 g. H$_2$O. Ca.	SO$_4$.	CO$_3$.
159°	0·210	0·208	0·058	0·131	0·006	206°	0·078	0·074	0·022	0·0358	0·012
159	0·212	0·208	0·059	0·130	0·007	206	0·072	0·070	—	0·0360	0·010
159	0·209	0·206	0·058	0·126	0·009	225	—	0·066	—	0·0302	0·012
159	0·208	0·209	0·060	0·128	0·012	225	0·048	0·048	—	0·0218	0·009
177	0·138	0·136	0·041	0·074	0·014	225	0·050	0·046	—	0·0214	0·008
179	0·139	0·139	0·041	0·079	0·012	241	0·040	0·036	—	0·0146	0·008
195	0·098	0·092	0·028	0·046	0·013	251	0·036	0·033	—	0·0132	0·008
195	0·092	0·091	—	0·050	0·009	252	0·030	0·030	—	0·0115	0·008
						252	0·032	0·031	—	0·0119	0·008

From Table I it will be seen that as the temperature rises the sulphate concentration falls, at first rapidly but later more slowly. The carbonate concentration at first rises slightly, but above about 200° it falls away. Over the whole of the temperature range the sulphate concentration is very much higher than the carbonate, so it is not surprising that the manner of the variation of sulphate concentration with temperature is much the same as it is in the two-component system CaSO$_4$–H$_2$O (Partridge, *op. cit.*, p. 43). On the other hand, the dissolved calcium carbonate is in the presence of a great excess of calcium ions (from the more soluble sulphate) and its behaviour as the temperature changes will be governed chiefly by the changes of the calcium concentration. Hence, at first as the temperature rises, the rapid fall in calcium sulphate concentration allows the calcium carbonate concentration to rise because of the great decrease in calcium-ion concentration. Later, the fall of calcium sulphate concentration with rise of temperature is not nearly so marked, and finally, as the metal-ion concentration becomes

TABLE II.

Solubility of (Calcium Sulphate + Calcium Carbonate).

(a) *In sodium sulphate solutions.*

G./1000 g. H$_2$O.

Temp.	Total solids. By evaptn.	By analysis.	Ca.	SO$_4$.	CO$_3$.	Na.	OH.	Na as Na$_2$SO$_4$ added.
159°	1·440	1·452	0·036	0·962	0·020	0·434	Nil	
159	1·467	1·477	0·040	0·983	0·020	0·434	Nil	
207	1·421	1·420	0·027	0·923	0·036	0·434	Nil	
206	1·374	1·365	0·016	0·880	0·035	0·434	Nil	1·339
225	1·358	1·371	0·010	0·872	0·055	0·434	Nil	
226	1·386	1·374	0·010	0·878	0·042	0·434	0·010	
259	1·351	1·338	0·0062	0·826	0·060	0·434	0·012	
257	1·369	1·379	0·0056	0·831	0·063	0·434	0·016	
159	2·803	2·822	0·038	1·886	0·030	0·868	Nil	
159	2·818	2·836	0·039	1·901	0·029	0·868	Trace	
207	2·748	2·758	0·014	1·821	0·053	0·868	0·002	2·678
207	2·733	2·736	0·013	1·800	0·055	0·868	Nil	
250	2·706	2·702	0·0067	1·741	0·072	0·868	0·014	
250	2·700	2·699	0·0070	1·738	0·074	0·868	0·012	
207	0·692	0·700	0·013	0·436	0·032	0·217	0·0042	
207	0·694	0·698	0·012	0·438	0·028	0·217	0·0030	0·670
250	0·672	0·663	0·0055	0·391	0·038	0·217	0·012	
250	0·676	0·661	0·0055	0·389	0·038	0·217	0·012	
250	0·276	0·262	0·0046	0·136	0·025	0·087	0·009	0·268
250	0·269	0·259	0·0050	0·133	0·024	0·087	0·010	

(b) *In sodium carbonate solutions.*

								Na as Na$_2$CO$_3$ added.
206	1·345	1·364	0·013	0·874	0·040	0·434	0·003	1·000
206	1·380	1·376	0·012	0·887	0·042	0·434	0·001	

steadier, the calcium carbonate concentration changes in the same way as it does in the system $CaCO_3$–H_2O, *i.e.*, it decreases as the temperature rises.

Table I gives evidence that the solubility of the carbonate alone in water is retrograde. By converting the concentration into g.-mols./1000 g. H_2O, and taking the mean values of [Ca], [SO_4], and [CO_3] at each temperature, the solubility products [$Ca^{..}$][SO_4''] and [$Ca^{..}$][CO_3''] can be calculated, by using the relation [CO_3''] + [SO_4''] = [$Ca^{..}$] where no calcium concentrations are given, and assuming practically complete ionisation. The square roots of the solubility products give the approximate solubilities of the single salts in water. Both decrease as the temperature rises, throughout the temperature range.

The accuracy of Table I appears to be about ± 10% for [SO_4] and ± 20% for [CO_3].

Table II (a) shows the effect of the addition of sodium sulphate. It will be seen that at equilibrium the composition of the solutions can be expressed as having practically the original amount of sodium sulphate with very little sodium carbonate. This is in agreement with the results of two experiments in which sodium carbonate was added, shown in Table II (b), and for which it was found that the solution at equilibrium contained principally sodium sulphate produced by double decomposition of sodium carbonate with calcium sulphate. It will be seen that the caustic alkalinity of the solutions was small, but increased fairly rapidly with temperature above 220°.

Table III shows the results obtained with sodium chloride solutions, and also with solutions containing both added chloride and sulphate.

TABLE III.

Solubility of (Calcium Sulphate + Calcium Carbonate) in Sodium Chloride (and Sodium Sulphate) Solutions.

G./1000 g. H_2O.

Temp.	Total solids. By evaptn.	By analysis.	Ca.	SO_4.	CO_3.	Cl.	Na.	OH.	NaCl.
159°	2·593	2·552	0·102	0·231	0·009	1·342	0·868	Nil	
159	2·562	2·545	0·102	0·228	0·009	1·338	0·868	„	
206	2·373	2·338	0·039	0·073	0·011	1·346	0·868	0·0008	
206	2·367	2·329	0·039	0·072	0·011	1·338	0·868	0·0008	2·207
250	2·345	2·303	0·019	0·0257	0·010	1·377	0·868	0·0017	
250	2·347	2·267	0·020	0·0263	0·009	1·342	0·868	0·0026	
207	1·233	1·205	0·031	0·055	0·012	0·673	0·434	Trace	1·103
206	1·231	1·205	0·032	0·056	0·012	0·671	0·434	0·0005	
206	2·521	2·488	0·012	0·898	0·035	0·673	0·868	0·0021	1·103 *
206	2·480	2·482	0·013	0·895	0·036	0·669	0·868	0·0013	
207	3·613	3·578	0·014	0·881	0·024	1·349	1·302	0·0076	2·207 *
206	3·632	3·590	0·014	0·897	0·030	1·342	1·302	0·0047	

* With addition of Na_2SO_4 (Na equiv. to 1·339 g. Na_2SO_4/1000 g. H_2O).

TABLE IV.

Solubility of (Calcium Sulphate + Calcium Carbonate) in Sodium Hydroxide Solutions.

G./1000 g. H_2O.

Temp.	Total solid by analysis.	Ca.	SO_4.	CO_3.	OH.	Na.	Na as NaOH.
159°	2·114	0·074	0·691	0·010	0·471	0·868	
159	2·111	0·074	0·683	0·015	0·471	0·868	
207	1·950	0·025	0·583	0·012	0·462	0·868	1·509
206	1·965	0·025	0·591	0·012	0·469	0·868	
250	1·950	0·0110	0·580	0·011	0·481	0·868	
159	1·108	0·088	0·278	0·011	0·297	0·434	
159	1·105	0·088	0·274	0·008	0·301	0·434	
207	0·945	0·029	0·191	0·015	0·276	0·434	0·754
207	0·948	0·028	0·193	0·020	0·273	0·434	
250	0·900	0·0110	0·163	0·008	0·285	0·434	
250	0·900	0·0110	0·161	0·013	0·282	0·434	
159	0·651	0·075	0·197	0·008	0·154	0·217	
160	0·648	0·075	0·193	0·009	0·154	0·217	
207	0·500	0·031	0·087	0·013	0·152	0·217	0·377
207	0·501	0·030	0·086	0·016	0·152	0·217	
250	0·446	0·0140	0·049	0·0065	0·159	0·217	
250	0·444	0·0135	0·049	0·0041	0·160	0·217	
160	3·220	0·068	0·210	0·018	0·615	1·309	2·263

Table IV shows the effect of sodium hydroxide.   It will be seen that at equilibrium the caustic alkalinity is appreciably less than that originally added, so that sodium sulphate has been formed. It has been suggested that the production of sulphate is due to double decomposition of caustic soda with calcium sulphate, with precipitation of calcium hydroxide.   This would account for the fall in the caustic alkalinity, but microscopic examinations of the solid phases from the equilibria with caustic soda solutions gave no indications of the presence of lime.

In Tables II, III, and IV, the calcium concentrations appear to be accurate to about 5% and the sulphate concentrations to about 1%, while the carbonate concentrations are given probably to 7% in Tables II and III and to about 20% in Table IV.

DISCUSSION.

The CO_3/SO_4 ratios shown in Tables V, VI (a), (b), (c), and (d) have been calculated from values for carbonate and sulphate concentrations interpolated from smooth curves drawn through plots of the experimental data.   The over-all accuracy is probably about 15%, although the data of Tables VI (a), (b), and (c) may be rather better than this.

TABLE V.

Carbonate and Sulphate Concentrations and Carbonate/Sulphate Ratios in the System $CaCO_3$– $CaSO_4$–H_2O, *at 160° to 250°.*

Temp.	Gauge, lbs./sq. in.	G./1000 g. H_2O. CO_3.	G./1000 g. H_2O. SO_4.	Ratio CO_3/SO_4 (g.).	Temp.	Gauge, lbs./sq. in.	G./1000 g. H_2O. CO_3.	G./1000 g. H_2O. SO_4.	Ratio CO_3/SO_4 (g.).
160°	75	0·0082	0·124	0·066	210°	262	0·0109	0·034	0·32
170°	101	0·0092	0·094	0·098	220°	322	0·0103	0·0272	0·38
180°	131	0·0102	0·072	0·142	230°	390	0·0095	0·0215	0·44
190°	168	0·0109	0·055	0·198	240°	470	0·0086	0·0167	0·51
200°	211	0·0110	0·043	0·26	250°	560	0·0077	0·0126	0·61

The ratios in the system $CaCO_3$–$CaSO_4$–H_2O between 160° and 250° are shown graphically in Fig. 2.   The broken line is a plot of theoretical values calculated by Hall's method

FIG. 2.
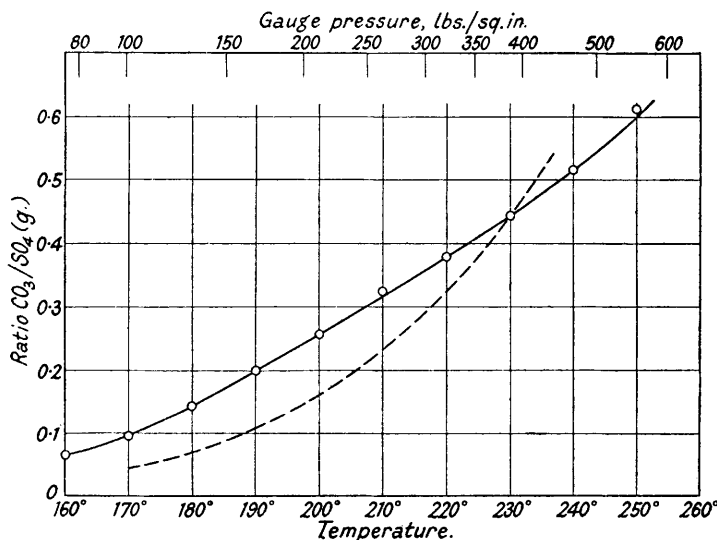
(cited by Jones, "Fuel Economy Review," 1932).   The agreement between the two is remarkable in view of the assumptions made in the calculation of the theoretical values. The theoretical values rise more rapidly with temperature than do the actual values in the three-component system, and exceed them above 230°.   This difference is apparently due to Hall's use of Kendall's solubilities for calcium carbonate, which increase with rising temperature : actually the solubility decreases.

<div align="center">TABLE VI.</div>

The Effect of Sodium Salts on the Carbonate and Sulphate Concentrations and CO_3/SO_4 Ratio by Additions to the System $CaCO_3$–$CaSO_4$–H_2O.

<div align="center">(Ratio = CO_3/SO_4 ratio in g. throughout.)</div>

(a) *Sodium sulphate.*

Temp.	Gauge, lbs./sq. in.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.
160°	75	0·0300	1·889	0·016	0·0203	0·970	0·021			
170	101	0·0338	1·873	0·018	0·0226	0·955	0·024			
180	131	0·0380	1·857	0·020	0·0252	0·940	0·027			
190	168	0·0427	1·840	0·023	0·0283	0·926	0·031			
200	211	0·0476	1·823	0·026	0·0317	0·911	0·035	0·0252	0·446	0·057
210	262	0·0523	1·806	0·029	0·0357	0·896	0·040	0·0277	0·432	0·064
220	322	0·0573	1·790	0·032	0·0402	0·882	0·046	0·0304	0·420	0·072
230	390	0·0625	1·774	0·035	0·0452	0·868	0·052	0·0332	0·409	0·081
240	470	0·0678	1·757	0·039	0·0506	0·853	0·059	0·0358	0·399	0·090
250	560	0·0734	1·740	0·042	0·0568	0·839	0·068	0·0383	0·390	0·098
260	665				0·0635	0·825	0·077			

Na equivalent to }   2·678 g. Na_2SO_4 per 1000 g. H_2O.   1·339 g. Na_2SO_4 per 1000 g. H_2O.   0·669 g. Na_2SO_4 per 1000 g. H_2O.

At 250° (gauge press. = 560 lbs./sq. in.), with Na equivalent to 0·268 g. Na_2SO_4/1000 g. H_2O : CO_3 = 0·0249, SO_4 = 0·134 g./1000 g. H_2O, ratio = 0·185.

(b) *Sodium sulphate + sodium chloride.*

206°	241	0·0359	0·897	0·040	0·0269	0·889	0·030

NaCl, g./1000 g. H_2O	1·103	2·207
Na_2SO_4, g./1000 g. H_2O	1·339	1·339

(c) *Sodium chloride* (2·207 g./1000 g. H_2O, except in last expt.).

Temp.	Gauge, lbs./sq. in.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.	Temp.	Gauge, lbs./sq. in.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.
160°	75	0·0092	0·226	0·041	220°	322	0·0107	0·052	0·206
170	101	0·0100	0·182	0·055	230	390	0·0104	0·042	0·248
180	131	0·0105	0·144	0·073	240	470	0·0100	0·033	0·303
190	168	0·0110	0·112	0·098	250	560	0·0095	0·026	0·365
200	211	0·0111	0·086	0·129	206 *	241	0·0118	0·056	0·211
210	262	0·0110	0·066	0·167					

<div align="center">* NaCl = 1·103 g./1000 g. H_2O.</div>

(d) *Sodium hydroxide.*

| Temp.	Gauge, lbs./sq. in.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.	G./1000 g. H_2O. CO_3.	SO_4.	Ratio.
160°	75	0·0103	0·685	0·015	0·0098	0·275	0·036	0·0087	0·195	0·045
170	101	0·0108	0·654	0·016	0·0125	0·255	0·049	0·0108	0·166	0·065
180	131	0·0111	0·628	0·018	0·0148	0·236	0·063	0·0126	0·140	0·090
190	168	0·0115	0·607	0·019	0·0165	0·218	0·076	0·0139	0·117	0·119
200	211	0·0116	0·593	0·020	0·0174	0·202	0·086	0·0145	0·097	0·149
210	262	0·0118	0·584	0·020	0·0174	0·188	0·092	0·0143	0·081	0·177
220	322	0·0117	0·580	0·020	0·0165	0·178	0·093	0·0132	0·068	0·193
230	390	0·0117	0·580	0·020	0·0151	0·170	0·089	0·0113	0·059	0·191
240	470	0·0115	0·580	0·020	0·0130	0·165	0·079	0·0086	0·052	0·165
250	560	0·0112	0·580	0·020	0·0104	0·162	0·064	0·0052	0·049	0·106

Na equivalent to }   1·509 g. NaOH per 1000 g. H_2O.   0·754 g. NaOH per 1000 g. H_2O.   0·377 g. NaOH per 1000 g. H_2O.

At 160° (gauge press. 75 lbs./sq. in.), with Na equivalent to 2·263 g. NaOH/1000 g. H_2O : CO_3 = 0·0184, SO_4 = 1·210 g./1000 g. H_2O, ratio = 0·015.

When sodium salts are added to the three-component system, it is not possible to represent fully the variation of the CO_3/SO_4 ratios by a graphical method. By making certain approximations, however, serviceable graphs can be constructed. By neglecting the small concentrations of sodium hydroxide present at equilibrium, the effect of sodium sulphate on the ratio can be expressed as in Fig. 3, where the ratio at 250°, 210°, and 160° is shown as a function of the total equilibrium SO_4 concentration, but reference should be

made to Table II for the precise compositions of the solutions. It will be seen at once that, when the solution contains appreciable quantities of sodium sulphate, neither Hall's theoretical values nor the ratios in the three-component system are even an approximation to the true state of affairs. Sodium sulphate lowers the ratio to a small fraction of that holding in the simple system at the same temperature, and also lowers the rate of increase

FIG 3.
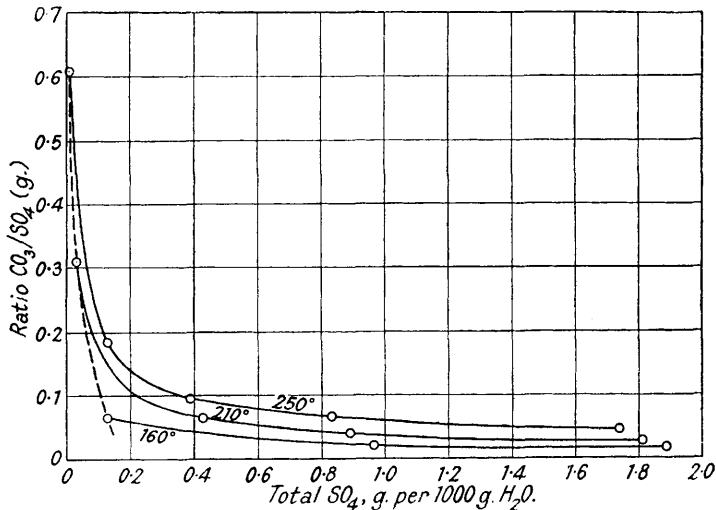
with temperature. It is clear, particularly at the higher temperatures, that the rate of lowering of the ratio with increasing SO_4 concentration decreases rapidly as the latter rises, so that at concentrations above 0·7 g. $SO_4/1000$ g. H_2O, the ratio, although very much less than that in the simple system, becomes roughly independent of the SO_4 concentration.
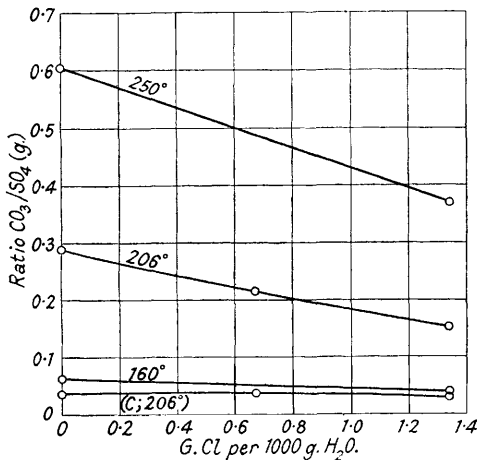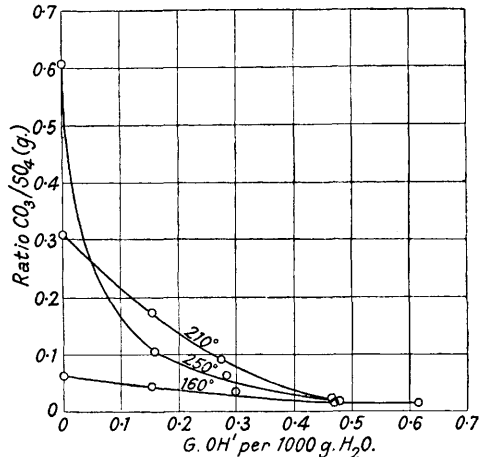
FIG. 4.   FIG. 5.

Fig. 4 shows the effect of sodium chloride at different temperatures. There is a lowering effect, but it is small compared to the effect of sodium sulphate, and the variation with temperature remains much the same as that in the simple system. In this figure is also shown (at C) the negligible effect on the CO_3/SO_4 ratio of the addition of sodium chloride to a solution containing 1·34 g. of added sodium sulphate per 1000 g. of H_2O, which has already lowered the ratio. From Table III it is seen that sodium chloride lowers the ratio by

increasing the calcium sulphate solubility, for the carbonate concentrations remain practically the same as in the simple system.

Fig. 5, which attempts to show the effect of sodium hydroxide, must be used only with reference to Table IV, which gives the full analyses of the solutions, since there is the complication that addition of the alkali brings about a great increase in the sodium sulphate concentration. The possibility of the production of solid calcium hydroxide from the caustic soda at the expense of calcium sulphate must also be kept in mind, particularly with regard to boiler practice, where the calcium sulphate is limited in quantity. In the present experimental work, large quantities of both calcium carbonate and sulphate were undoubtedly present as solid phases at equilibrium, so that it is possible to give the true CO_3/SO_4 ratio for solutions of the compositions given in Table IV. Due allowance must be made for the increased sulphate concentration which accompanies the caustic soda. Thus, Fig. 5 shows the ratio to be 0·019 at 250° with a concentration of 0·48 g. of OH' per 1000 g. of H_2O, but the sulphate concentration associated with this, 0·58 g./1000 g. H_2O, would alone suffice to reduce the ratio to 0·08 from its value of 0·6 in the simple system. For the reasons which have been given, it is difficult to assess the quantitative effect of hydroxide alone on the CO_3/SO_4 ratio; all that can be said is that it appears to lower it more than does sodium chloride. In practice an OH concentration unaccompanied by an appreciable SO_4 concentration is not likely to be encountered.

These conclusions are further supported by Straub's recent work, (" The Cause and Prevention of Calcium Sulphate Scale in Steam Boilers," Bulletin No. 261, 1933, Engineering Experiment Station, University of Illinois). Examination of his results, however, shows that he has not made a systematic determination of the CO_3/SO_4 ratios for the co-existence of the two solid phases calcium carbonate and calcium sulphate, since he took no steps to ensure that *both* solid phases were present together in the equilibria he studied. His results give the compositions of various solutions in equilibrium with either one or the other, but do not show the *minimum* CO_3/SO_4 ratios for the prevention of calcium sulphate precipitation.

SUMMARY.

Carbonate/sulphate ratios have been determined in solutions in equilibrium with the co-existing solid phases calcium carbonate (calcite) and calcium sulphate (anhydrite).

In the system $CaCO_3$–$CaSO_4$–H_2O between 159° and 252°, the ratios found by experiment increase less rapidly with temperature than do those calculated by previous workers, and above 230° are lower than these calculated figures.

The effect on the CO_3/SO_4 ratio of low concentrations of dissolved sodium salts has also been studied. The ratio is reduced greatly by sodium sulphate, and much less effectively by sodium chloride. When sodium hydroxide is added to the three-component system, an appreciable concentration of sodium sulphate is found at equilibrium; the greatly lowered CO_3/SO_4 ratio in these alkaline solutions is principally brought about by the sodium sulphate formed, but is in part due to sodium hydroxide.