TABLE I

	H_2SO_4 (96%)	Na_2SO_4	NaOH	Na_2SO_4
Solutes, g.	9.125	2.10	2.84	1.68
Water, g.	9.93	5.00	4.00	
% O^{18} in water	0.79	0.79	0.84	
% O^{18} in water of orig. soln. (calcd.)	0.77	0.79	0.675	
Temp., °C.	100	100	100	
Time (hrs.)	59	87	84	
Vessel	Pyrex	Pyrex	Platinum	
% O^{18} in water recovered	0.55	0.79	0.67	
Obsd. decr. in % O^{18}	0.22	0.00	0.005	
% decr. calcd. for compl. exch.	0.22	0.11	0.06	
Amt. of exch.	Complete	None	None	

We also agree with Winter, Carlton and Briscoe for alkaline solution, but disagree with Datta, Day and Ingold.

Partial exchange has been observed for potassium acid sulfate by Titani and Goto and by Mills.[7] Winter, Carlton and Briscoe observed no exchange of sulfate in acid solution, but we must disagree with this observation.

Our results, coupled with those of Mills for potassium acid sulfate, lead us to postulate, as the mechanism for the exchange of sulfate, the same type of reversible anhydride formation which has satisfactorily accounted for the exchange of carbonate under all conditions of acidity.[8] The difference in the rates appears to be chiefly due to the fact that sulfuric acid is a stronger acid than carbonic, and that a much smaller quantity of the anhydride is present in solution.

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(7) Mills, THIS JOURNAL, **62**, 2833 (1940).

(8) Mills and Urey, *ibid.*, **62**, 1019 (1940).

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Density of Perchloric Acid Solutions

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Data in the literature on the density of perchloric acid cover only a limited range of concentration. In this work, the density at 25° has been determined over the range up to 65% concentration. Measurements were in a 25-cc. pycnometer, the volume found by weighing filled with water, weights reduced to vacuum. The solutions were made from a stock solution of C. P. acid, meeting A. C. S. specifications. Its concentration was found by density and the data of Smith and Goehler[1] to be 71.209%. Titration confirmed this concentration.

The estimated maximum error, based on the differences of duplicate determinations, is about five in the last figure.

Measurements at 30° at intervals of 10% give a basis for estimating the temperature coefficient of density, over the range 25° to 30°. Empirically, $\Delta d/\Delta t = -(28 + 1.4x)10^{-5}$ in which x is the per cent. of acid.

The empirical equation which most nearly fits these data is:

$$d^{25}_4 = 0.99707 + 0.00562796x + 0.0000230045x^2 + 0.00000049593x^3$$

The maximum deviations of this equation over portions of the concentration range are:

Range	Maximum error in d^{25}_4	Maximum error in x
0 – 20%	0.00027	0.045
20 – 40	0.00006	0.006
40 – 65	0.00298	0.222

Wt. per cent. acid	d^{25}_4	d^{30}_4
0	(0.99707)	(0.99568)
1	1.00265	
2	1.00828	
4	1.01975	
6	1.03154	
8	1.04355	
10	1.05591	1.05388
12	1.06862	
14	1.08163	
16	1.09498	
18	1.10866	
20	1.12280	1.11999
22	1.13734	
24	1.15224	
26	1.16761	
28	1.18359	
30	1.20002	1.19651
32	1.21697	
34	1.23446	
36	1.25259	
38	1.27130	
40	1.29073	1.28658
45	1.34252	
50	1.39937	1.39435
55	1.46134	
60	1.52766	1.52177
65	1.59628	

The value which Smith and Goehler gave for the density at 65% concentration was 1.59665. This value was found by interpolation between two points at some distance apart, using a straight line. Since the analysis of the acid used depends on their data, closer agreement than this with

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(1) Smith and Goehler, *Ind. Eng. Chem., Anal. Ed.*, **3**, 61 (1931).

their other points should be expected. Their use of a straight line over the range 63–70% seems poorly justified, since there were no experimental points in this range. In the range 70–75% the straight line they used is supported by a number of points. The stock acid used in this work was in this range of concentration. It should be noted that while the difference in density figures at 65% is rather large, it corresponds to a difference in acid concentration of about 0.027%.

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A Note on the Phase Rule Diagram for a Mixture of Sodium Palmitate and Sodium Laurate with Water

By J. W. McBain and S. A. Johnston

The temperatures above which mixtures of soap and water in various proportions form isotropic solutions, T_i, and the temperatures below which they contain soap curd, T_c, have been determined for most of the single pure soaps. It is therefore of interest to see how these are affected when two such soaps are mixed. For this purpose a constant mixture of equal weights of sodium palmitate and sodium laurate has been examined with different percentages of water, using the materials and technique of previous communications.[1]

Briefly, this consisted in preparing sealed Pyrex tubes containing the mixture with varying amounts of water. The contents of the tubes were homogenized by heating to a high temperature, around 300° in this case. If the tube was then cooled slowly a temperature was reached at which another phase separated. This phase is frequently anisotropic and may be recognized even in minute quantities by observing the solution through crossed Polaroids. These points form the T_i curve. The tubes were then cooled to room temperature and heated slowly. The temperature at which the white curdiness disappeared was noted and these temperatures form what is usually called the T_c curve.

The results are given in Fig. 1 for the mixture where also the positions of middle soap, neat soap and curd are indicated. Figure 1 also compares these results with those of the separate single soaps, represented by faint lines. A comparison of the curves shows that the mixture tends to follow a behavior which would be an average of the individual curves. Probably the outstanding difference is that the peak for middle soap is higher than either of the individual peaks and if anything is nearer the peak for sodium palmitate. The T_c curve, on the other hand, adheres more closely to the curve for sodium laurate, as might be expected from previous experience.[1a,1c] Mixed micelles of smaller size, less orientation and greater solubility, must be produced by the occurrence of the shorter laurate molecules amongst the longer homologs, an example of mutual solubilization.

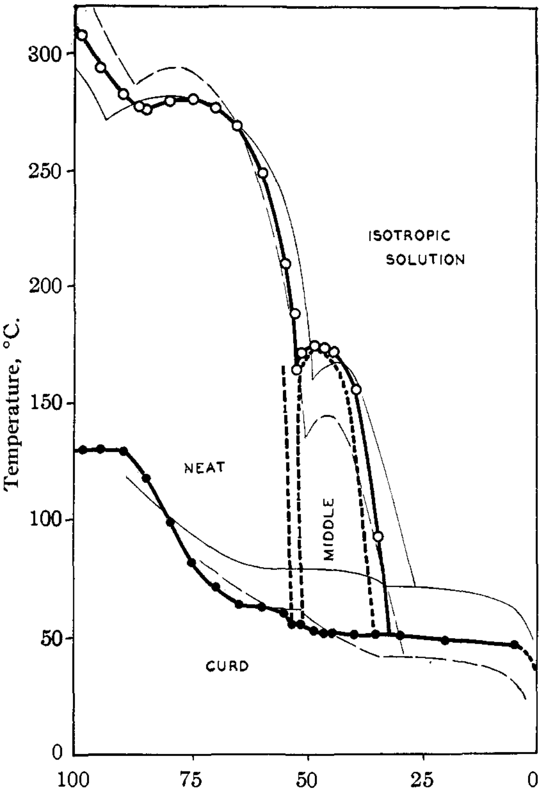

Fig. 1.—○, T_i curve; ●, T_c curve; ———, NaP; - - -, NaL.

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[1] (a) McBain, Lazarus and Pitter, *Z. physik. Chem.*, **A147**, 87, 116 (1930); (b) McBain, Brock, Vold and Vold, This Journal, **60**, 1870 (1938); (c) McBain, Vold and Jameson, *ibid.*, **61**, 30 (1939); (d) Vold, *J. Phys. Chem.*, **43**, 1213 (1939).

The Effect of Potassium Oleate upon the Solubility of Hydrocarbon Vapors in Water

By J. W. McBain and J. J. O'Connor

Solubilization by colloidal electrolytes and other detergents is best studied in systems where there