the normality of all the tyrosyl and carboxyl groups in denaturing solvents,[18,21] the possible existence of tyrosyl–carboxylate ion hydrogen bonds,[22] the results of Richards[23] on the relationship between the N-terminal tail and biological function, etc. A summary of current structural information on ribonuclease has been presented by Linderstrøm-Lang and Schellman.[24]

If tyrosyl–carboxylate ion hydrogen bonds play any significant role in stabilizing the folded configuration, the loss of this stabilization should be evident at *p*H 1.0. However, our results indicate that exposure to *p*H 1.0 produces a significant loss of folding only after an irreversible change has taken place in the molecule.

Finally, the data of Fig. 1 indicate that ribonuclease III has a greater degree of hydrogen-shielding since a larger fraction of its hydrogens do not exchange in 20 hr. at 0° than was observed for the other forms of ribonuclease. Whether or not ribonuclease III has a greater degree of helical character remains to be seen. Aside from kinetic factors affecting the rate of transformation of one configuration into another, the solvent also influences the equilibrium configuration. Therefore, it is not at all surprising that variation of solvent (*i.e.*, crystallizing medium) can change the equilibrium configuration of the molecule from one form to another.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Thermodynamic Properties of Aqueous Sulfuric Acid Solutions and Hydrates from 15 to 300°K.[1]

BY W. F. GIAUQUE, E. W. HORNUNG, J. E. KUNZLER AND T. R. RUBIN

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The heat capacities, entropies, free energies and heat contents of all stable phases in the H_2SO_4–H_2O system are correlated and tabulated from 15 to 300°K. Ice is known to have frozen-in disorder at low temperatures and thus is unstable. Sulfuric acid and all of its hydrates approach perfectly ordered crystalline states at low temperatures as is indicated by the complete entropy agreements. The stable phases are H_2SO_4, $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, $H_2SO_4 \cdot 3H_2O$, $H_2SO_4 \cdot 4H_2O$ and $H_2SO_4 \cdot 6.5H_2O$. The various phases are connected by means of thermodynamic properties of the liquid solutions at 298.15°K. (25°). At this temperature values of the partial molal free energies, heat contents, heat capacities and some values for the change of heat capacity with temperature are given. The activity of water is tabulated at concentrations up to pure H_2SO_4, where $a_{H_2O} = 1.56 \times 10^{-9}$. Pure H_2SO_4 is used as a reference zero for most of the properties; however, values of the activity coefficient in the ordinary hypothetically molal reference system are given up to 1000 molal. The activity of pure H_2SO_4 in this system is 3.41×10^9 ($m = \infty$). It is concluded that no intermediate hydrate becomes unstable with respect to a higher and lower hydrate. This statement also includes ice and pure sulfuric acid. It is pointed out that such functions as free energy/temperature, heat content/temperature, heat capacity and entropy need a common and short name for their common unit, defined cal. deg.$^{-1}$. The name should not be one which has applied particularly to any one of these properties. The use of the short name Gibbs is suggested, thus 1 gibbs (g. mole)$^{-1}$ = 1 gbs. (g. mole)$^{-1}$ = 1 defined cal. (°K.)$^{-1}$ (g. mole)$^{-1}$ = 1 defined B.t.u. (°R)$^{-1}$ (lb. mole)$^{-1}$.

This paper correlates an extensive series of researches on aqueous sulfuric acid. Throughout the publication of the numerous papers in this series we have omitted tables of smoothed data because it was felt desirable to have all of the thermodynamic properties correlated and in one place. This also adds considerably to the efficiency of the presentation. Much of the original data has been recalculated in order to eliminate errors as completely as possible before the data were used to derive the new results presented here, such as the partial molal free energies and absolute partial molal entropies of the components.

The measurements have been particularly designed to give information in the concentration range from several molal to the anhydrous acid and over the entire temperature region below 300°K. In addition to the anhydrous acid and ice, the solid phases known at low temperatures are the mono-, di-, tri-, tetra- and hemihexa(6.5)-hydrates. A solid believed to be octahydrate exists but we did not succeed in cooling it to low temperatures. The original objective was to make use of the third law of thermodynamics to find out if the acid or any of its hydrates retained disorder at limiting low temperatures, due to random hydrogen bonding or other effects leading to lack of internal crystalline perfection.

In starting this problem it was hoped that most of the data needed to calculate the entropies of formation of the several hydrates from each other at ordinary temperatures were already available. We were soon disillusioned. We do not mean to imply that previous work on aqueous sulfuric acid does not include many examples of very good work but rather that the significant application of the equation

$$\Delta S = (\Delta H - \Delta F)/T$$

to the present problem requires data of very great accuracy. For example a combined error of the order of 100 cal. mole^{-1} in ($\Delta H - \Delta F$) at 298°K. leads to an error of several tenths of a cal. deg.$^{-1}$ mole^{-1} in ΔS, and this small amount can have significance in theoretical explanations of disorder in crystals. We may say at once that no evidence of residual disorder at low temperatures

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TABLE I

RELATIVE PARTIAL MOLAL FREE ENERGIES, HEAT CONTENTS, ENTROPIES AND HEAT CAPACITIES OF AQUEOUS SULFURIC ACID AT 25° (298.15°K.)

SECTION I

$S_1^0 = 16.710$, $S_2^0 = 37.501$ cal. deg.$^{-1}$ mole^{-1}

A $\frac{\text{moles } H_2O}{\text{moles } H_2SO_4}$	H_2SO_4, wt. %	$\bar{F}_1^0 - \bar{F}_1$	$\bar{F}_2^0 - \bar{F}_2$	$-\bar{L}_1$	$-\bar{L}_2$	$\bar{S}_1$	$\bar{S}_2$
			cal. mole^{-1}			cal. deg.$^{-1}$ mole^{-1}	
−0.15	102.833			17,148	−2.9		
− .10	101.871			17,180	+1.1		
− .05	100.927			17,203	2.9		
− .04	100.740			17,205	3.0		
− .03	100.554			17,203	2.95		
− .020	100.369			17,194	2.74		
− .015	100.276			17,184	2.57		
− .010	100.184			17,164	2.32		
− .009	100.166			17,155	2.24		
− .008	100.147			17,141	2.18		
− .007	100.129			17,118	1.95		
− .006	100.110			17,083	1.72		
− .005	100.092	13,374	2.56	17,033	1.45	4.438	37.505
− .004	100.074	13,232	1.92	16,966	1.15	4.187	37.504
− .003	100.055	13,049	1.28	16,874	0.83	3.881	37.503
− .002	100.037	12,809	0.687	16,737	.49	3.535	37.502
− .001	100.018	12,489	.215	16,518	.17	3.197	37.501
.000	100.000	12,014	.000	16,125	.00	2.922	37.501
.001	99.982	11,460	.250	15,200	.52	4.166	37.500
.002	99.963	11,099	.780	13,500	3.10	8.657	37.493
.003	99.945	10,838	1.437	11,575	7.87	14.238	37.479
.004	99.927	10,618	2.19	10,325	12.2	17.693	37.467
.005	99.908	10,423	3.07	9,575	15.5	19.554	37.459
.006	99.890	10,248	4.03	9,125	18.0	20.477	37.454
.007	99.872	10,092	5.04	8,835	19.9	20.926	37.451
.008	99.853	9,954	6.08	8,655	21.2	21.067	37.450
.009	99.835	9,831	7.13	8,515	22.4	21.124	37.450
.010	99.817	9,720	8.18	8,415	23.4	21.087	37.450
.015	99.725	9,295	14.33	8,110	27.1	20.685	37.458
.020	99.634	8,997	18.59	7,985	29.2	20.104	37.465
.03	99.452	8,579	28.89	7,905	31.0	18.971	37.494
.04	99.270	8,284	39.17	7,876	32.2	18.078	37.524
.05	99.090	8,054	49.49	7,855	33.3	17.377	37.555
.10	98.196	7,318	102.4	7,739	42.1	15.298	37.703
.15	97.319	6,873	157.8	7,618	57.2	12.211	37.838
.20	96.457	6,541	215.7	7,497	78.4	13.504	37.962
.25	95.610	6,268	276.9	7,376	105.6	12.994	38.076
.30	94.777	6,031	341.6	7,255	138.9	12.605	38.181
.35	93.959	5,820	409.8	7,133	178.5	12.306	38.277
.40	93.156	5,630	481.5	7,008	225.4	12.088	38.360
.45	92.365	5,454	556.6	6,880	280	11.927	38.429
.50	91.588	5,287	635.5	6,743	345	11.827	38.476
.55	90.824	5,128	719	6,592	424	11.800	38.489
.60	90.073	4,973	808	6,434	515	11.810	38.483
.65	89.334	4,824	902	6,275	614	11.843	38.467
.70	88.607	4,678	1,000	6,103	731	11.931	38.403
.75	87.892	4,535	1,103	5,906	874	12.112	38.269
.80	87.188	4,397	1,211	5,694	1,038	12.360	38.081
.85	86.495	4,262	1,322	5,476	1,218	12.638	37.850
.90	85.814	4,130	1,437	5,258	1,409	12.927	37.595
.95	85.143	4,002	1,555	5,039	1,611	13.232	37.313
1.00	84.482	3,878	1,677	4,819	1,826	13.554	37.001
1.05	83.832	3,757	1,800	4,599	2,051	13.886	36.659
1.10	83.191	3,640	1,926	4,387	2,279	14.205	36.317
1.15	82.560	3,527	2,054	4,186	2,505	14.500	35.988
1.20	81.939	3,417	2,183	3,997	2,727	14.765	35.676
1.25	81.327	3,311	2,312	3,821	2,943	14.999	35.385
1.30	80.724	3,209	2,442	3,657	3,151	15.206	35.123
1.35	80.130	3,111	2,572	3,507	3,350	15.381	34.892
1.40	79.545	3,018	2,701	3,367	3,542	15.538	34.680
1.45	78.968	2,928	2,829	3,238	3,726	15.669	34.492

TABLE I (*continued*)

A $\frac{\text{moles } H_2O}{\text{moles } H_2SO_4}$	H_2SO_4, wt. %	$\bar{F}_1^0 - \bar{F}_1$	$\bar{F}_2^0 - \bar{F}_2$ cal. mole^{-1}	$-\bar{L}_1$	$-\bar{L}_2$	$\bar{S}_1$ cal. deg.$^{-1}$ mole^{-1}	$\bar{S}_2$
1.50	78.399	2,842	2,955	3,118	3,903	15.783	34.321
1.55	77.839	2,760	3,080	3,007	4,073	15.882	34.170
1.60	77.286	2,682	3,203	2,904	4,236	15.967	34.036
1.65	76.741	2,607	3,325	2,807	4,393	16.040	33.919
1.70	76.204	2,535	3,446	2,716	4,545	16.102	33.815
1.75	75.675	2,466	3,564	2,631	4,692	16.158	33.718
1.80	75.152	2,400	3,681	2,550	4,836	16.208	33.627
1.85	74.637	2,337	3,796	2,473	4,975	16.253	33.547
1.90	74.129	2,276	3,910	2,401	5,111	16.292	33.473
1.95	73.628	2,218	4,022	2,332	5,244	16.328	33.402
2.00	73.133	2,162	4,134	2,267	5,373	16.359	33.345
2.1	72.164	2,055.8	4,351	2,145.5	5,622	16.409	33.238
2.2	71.220	1,956.8	4,564	2,035.4	5,859	16.446	33.158
2.3	70.300	1,864.9	4,771	1,934.8	6,085	16.476	33.094
2.4	69.404	1,778.5	4,974	1,842.7	6,301	16.495	33.050
2.5	68.530	1,697.8	5,171	1,757.9	6,509	16.508	33.013
2.6	67.678	1,622.3	5,364	1,679.7	6,708	16.517	32.993
2.7	66.847	1,551.8	5,551	1,607.2	6,900	16.524	32.976
2.8	66.037	1,486.0	5,732	1,539.9	7,085	16.529	32.963
2.9	65.245	1,424.3	5,908	1,477.3	7,264	16.532	32.953
3.0	64.472	1,366.2	6,079	1,418.9	7,436	16.533	32.950
3.1	63.718	1,312.0	6,244	1,364.3	7,602	16.535	32.946
3.2	62.981	1,261.2	6,404	1,313.0	7,764	16.536	32.940
3.3	62.261	1,213.5	6,559	1,264.7	7,921	16.538	32.933
3.4	61.557	1,168.7	6,709	1,219.3	8,073	16.540	32.926
3.5	60.868	1,126.7	6,854	1,176.7	8,220	16.542	32.919
3.6	60.195	1,087.1	6,994	1,136.4	8,363	16.545	32.909
3.7	59.537	1,049.7	7,131	1,098.3	8,502	16.547	32.903
3.8	58.893	1,014.3	7,264	1,062.3	8,637	16.549	32.896
3.9	58.263	980.6	7,393	1,028.1	8,769	16.551	32.886
4.0	57.646	948.6	7,520	995.7	8,897	16.552	32.883
4.25	56.159	875.6	7,821	921.7	9,202	16.555	32.869
4.50	54.747	810.6	8,105	855.8	9,490	16.558	32.856
4.75	53.405	752.6	8,373	797.2	9,761	16.560	32.846
5.00	52.126	700.5	8,627	744.5	10,018	16.562	32.836
5.25	50.908	653.7	8,867	696.7	10,262	16.566	32.822
5.50	49.745	611.6	9,093	653.5	10,495	16.569	32.799
5.75	48.634	573.3	9,308	613.8	10,718	16.574	32.772
6.00	47.572	538.8	9,511	577.4	10,932	16.581	32.735
6.25	46.555	507.5	9,703	543.6	11,139	16.589	32.685
6.50	45.580	478.8	9,885	512.4	11,338	16.597	32.628
6.75	44.646	452.5	10,060	483.2	11,531	16.607	32.567
7.00	43.749	428.4	10,225	456.1	11,717	16.617	32.497
7.5	42.059	385.6	10,535	406.5	12,077	16.640	32.329
8.0	40.495	349.0	10,819	362.5	12,417	16.665	32.141
8.5	39.043	317.4	11,079	324.0	12,735	16.688	31.947
9.0	37.691	290.1	11,318	290.0	13,032	16.710	31.752
9.5	36.430	266.4	11,537	260.1	13,308	16.731	31.561
10	35.251	245.6	11,740	233.8	13,565	16.750	31.380
11	33.107	211.5	12,097	190.4	14,020	16.781	31.051
12	31.209	184.5	12,407	156.0	14,415	16.806	30.766
13	29.517	163.0	12,676	128.6	14,757	16.825	30.521
14	27.999	145.2	12,915	106.7	15,052	16.839	30.333
15	26.629	130.7	13,126	89.2	15,305	16.849	30.193
17.5	23.728	103.7	13,564	59.9	15,778	16.857	30.075
20	21.397	85.04	13,910	42.5	16,102	16.853	30.149
22.5	19.482	71.79	14,191	31.18	16,342	16.846	30.287
25	17.882	61.99	14,423	23.70	16,519	16.838	30.471
27.5	16.525	54.56	14,617	18.68	16,650	16.830	30.682
30	15.360	48.69	14,786	15.29	16,748	16.822	30.920
35	13.461	39.97	15,068	11.21	16,879	16.806	31.427
40	11.980	33.79	15,299	8.78	16,970	16.794	31.896
45	10.792	29.25	15,491	7.18	17,037	16.784	32.316
50	9.819	25.81	15,654	6.10	17,088	16.776	32.691
55.506	8.932	22.84	15,811	5.29	17,138	16.769	33.050
∞	0	0	∞	0		16.710	∞

TABLE I

SECTION 2

A	C_p, cal. deg.$^{-1}$ g.$^{-1}$	$\bar{C}_p$ cal. deg.$^{-1}$ mole^{-1}	$\bar{C}_{p2}$ cal. deg.$^{-1}$ mole^{-1}	dC_p/dT, cal. deg.$^{-2}$ g.$^{-1}$ $\times 10^6$	$d\bar{C}_{p1}/dT$ cal. deg.$^{-2}$ mole^{-1}	$d\bar{C}_{p2}/dT$ cal. deg.$^{-2}$ mole^{-1}
−0.15	0.3233	11.80	32.61			
− .10	.3265	11.96	32.63			
− .05	.3298	13.13	32.71			
− .04	.3306	13.70	32.74			
− .03	.3314	14.61	32.77			
− .020	.3324	16.8	32.82			
− .015	.3330	19.8	32.87			
− .010	.3339	27.0	32.96			
− .009	.3341	29	32.98			
− .008	.3344	31	33.00			
− .007	.3346	34	33.02			
− .006	.3349	38	33.04			
− .005	.3353	42	33.07			
− .004	.3357	47	33.09			
− .003	.3361	55	33.12			
− .002	.3367	68	33.15			
− .001	.3374	90	33.18			
0	.3385	...	33.20	519	0.000	0.0509
0.001	.3373	−59	33.15	519	.000	.0509
.002	.3367	−40	33.12	519	.000	.0509
.003	.3364	−29	33.10	519	− .001	.0509
.004	.3360	−22	33.07	519	− .001	.0509
.005	.3357	−17	33.05	518	− .002	.0509
.006	.3355	−13.5	33.02	518	− .002	.0509
.007	.3353	−10.9	33.01	518	− .002	.0509
.008	.3351	− 8.8	32.99	518	− .002	.0509
.009	.3350	− 7.0	32.97	518	− .003	.0509
.010	.3349	− 5.4	32.96	518	− .003	.0509
.015	.3345	+ 0.2	32.90	517	− .004	.0509
.020	.3343	3.8	32.83	516	− .006	.0509
.03	.3343	7.8	32.74	515	− .008	.0509
.04	.3346	9.8	32.67	513	− .011	.0511
.05	.3351	10.8	32.63	512	− .013	.0513
.10	.3379	12.84	32.47	497	− .022	.0518
.15	.3417	14.49	32.26	480	− .0292	.0527
.20	.3461	15.94	32.01	461	− .0346	.0538
.25	.3512	17.22	31.72	440	− .0384	.0547
.30	.3567	18.35	31.41	416	− .0411	.0553
.35	.3627	19.36	31.08	391	− .0429	.0558
.40	.3690	20.28	30.74	368	− .0436	.0562
.45	.3756	21.12	30.38	344	− .0432	.0560
.50	.3825	21.85	30.04	321	− .0418	.0552
.55	.3895	22.42	29.74	300	− .0390	.0538
.60	.3967	22.75	29.55	280	− .0350	.0514
.65	.4038	22.80	29.52	263	− .0292	.0479
.70	.4108	22.57	29.67	249	− .0211	.0423
.75	.4175	22.03	30.07	242	− .0102	.0347
.80	.4238	21.17	30.73	237	+ .0058	.0220
.85	.4295	20.00	31.70	248	.0348	− .0015
.90	.4345	18.55	32.97	266	.0790	− .0407
.95	.4388	16.86	34.54	306	.1208	− .0795
1.00	.4423	15.06	36.29	361	.1300	− .0881
1.05	.4450	13.37	38.02	407	.1198	− .0781
1.10	.4469	11.96	39.54	455	.0962	− .0522
1.15	.4483	10.95	40.67	486	.0738	− .0272
1.20	.4494	10.31	41.42	510	.0550	− .0049
1.25	.4502	9.95	41.86	525	.0388	+ .0149
1.30	.4509	9.79	42.06	535	.0254	.0320
1.35	.4516	9.76	42.10	541	.0136	.0476
1.40	.4523	9.84	41.99	539	.0033	.0660
1.45	.4530	10.00	41.77	534	− .0058	.0748
1.50	.4538	10.20	41.47	526	− .0137	.0864
1.55	.4546	10.39	41.18	516	− .0201	.0962
1.60	.4555	10.57	40.90	503	− .0251	.1040
1.65	.4565	10.76	40.59	489	− .0290	.1104
1.70	.4575	10.94	40.29	474	− .0321	.1155
1.75	.4586	11.13	39.96	458	− .0343	.1193
1.80	.4597	11.320	39.62	441	− .0356	.1216
1.85	.4609	11.514	39.27	424	− .0362	.1227
1.90	.4622	11.711	38.90	408	− .0360	.1223
1.95	.4635	11.911	38.51	392	− .0352	.1208
2.0	.4648	12.111	38.12	376	− .0340	.1184
2.1	.4677	12.507	37.31	347	− .0303	.1109
2.2	.4708	12.896	36.47	322	− .0263	.1023

TABLE I (*continued*)

A	C_p, cal. deg.$^{-1}$ g.$^{-1}$	$\bar{C}_{p1}$ cal. deg.$^{-1}$ mole^{-1}	$\bar{C}_{p2}$ cal. deg.$^{-1}$ mole^{-1}	dC_p/dT, cal. deg.$^{-2}$ g.$^{-1}$ $\times 10^6$	$d\bar{C}_{p1}/dT$ cal. deg.$^{-2}$ mole^{-1}	$d\bar{C}_{p2}/dT$ cal. deg.$^{-2}$ mole^{-1}
2.3	.4741	13.274	35.62	301	− .0221	.0928
2.4	.4776	13.638	34.76	283	− .0178	.0827
2.5	.4812	13.980	33.93	268	− .0136	.0724
2.6	.4850	14.296	33.12	257	− .0097	.0625
2.7	.4889	14.586	32.35	248	− .0063	.0535
2.8	.4929	14.853	31.62	242	− .0031	.0447
2.9	.4969	15.101	30.91	238	− .0002	.0364
3.0	.5011	15.329	30.24	236	+ .0024	.0287
3.1	.5052	15.540	29.60	236	.0047	.0217
3.2	.5094	15.730	29.00	237	.0067	.0154
3.3	.5136	15.901	28.44	239	.0084	.0099
3.4	.5179	16.053	27.93	242	.0097	.0055
3.5	.5221	16.186	27.47	245	.0106	.0024
3.6	.5263	16.302	27.06	249	.0114	− .0004
3.7	.5304	16.405	26.69	254	.0120	− .0026
3.8	.5346	16.497	26.34	258	.0124	− .0041
3.9	.5387	16.581	26.02	263	.0129	− .0060
4.0	.5427	16.657	25.72	268	.0133	− .0076
4.25	.5527	16.829	25.01	281	.0143	− .0117
4.50	.5625	16.993	24.30	295	.0155	− .0170
4.75	.5718	17.162	23.50	309	.0170	− .0239
5.00	.5811	17.352	22.58	326	.0190	− .0337
5.25	.5902	17.562	21.51	344	.0213	− .0455
5.50	.5991	17.782	20.32	365	.0238	− .0589
5.75	.6079	17.995	19.13	388	.0259	− .0707
6.00	.6166	18.187	18.00	412	.0273	− .0789
6.25	.6251	18.348	17.02	436	.0276	− .0807
6.50	.6334	18.468	16.26	458	.0264	− .0731
6.75	.6414	18.544	15.74	477	.0239	− .0565
7.0	.6493	18.592	15.42	493	.0212	− .0379
7.5	.6641	18.642	15.05	513	.0172	− .0094
8.0	.6779	18.660	14.92	528	.0164	− .0033
8.5	.6907	18.660	14.92	542	.0167	− .0058
9.0	.7027	18.640	15.10	556	.0169	− .0075
9.5	.7138	18.613	15.35	569	.0174	− .0121
10	.7241	18.567	15.80	582	.0177	− .0150
11	.7425	18.429	17.25	607	.0180	− .0181
12	.7583	18.248	19.33	630	.0182	− .0204
13	.7718	18.057	21.72	652	.0190	− .0305
14	.7834	17.891	23.96			
15	.7935	17.806	25.18			
17.5	.8146	17.769	25.77			
20	.8315	17.771	25.72			
22.5	.8454	17.777	25.61			
25	.8570	17.783	25.45			
27.5	.8669	17.791	25.25			
30	.8754	17.800	24.98			
35	.8894	17.820	24.33			
40	.9004	17.840	23.58			
45	.9094	17.858	22.81			
50	.9168	17.875	22.01			
55.506	.9238	17.896	21.03			
∞	.9989	17.996	...			

Many of the values in Table I are given to an extra figure to preserve relative accuracy and the Duhem relationship of the partial molal properties.

has been found in sulfuric acid or any of its hydrates.

The sources of measurements for the tables of thermodynamic properties to be given below are as follows: The heat capacities of H_2SO_4, $H_2SO_4 \cdot H_2O$ and $H_2SO_4 \cdot 2H_2O$ from 15 to 300°K. have been measured by Rubin and Giauque.[2] The heat capacities of $H_2SO_4 \cdot 3H_2O$ and $H_2SO_4 \cdot 4H_2O$ over the same temperature interval are from Hornung and Giauque.[3] The heat capacity of $H_2SO_4 \cdot 6.5H_2O$ to 300°K. has been determined by Hornung, Brackett and Giauque,[4] who also comment on $H_2SO_4 \cdot 8H_2O$.

Since molality cannot be used over the range of concentration to pure sulfuric acid, it will be convenient to use A, the number of moles of water per mole of sulfuric acid. Pure

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[2] T. R. Rubin and W. F. Giauque, THIS JOURNAL, **74**, 800 (1952).

[3] E. W. Hornung and W. F. Giauque, *ibid.*, **77**, 2983 (1955).

[4] E. W. Hornung, T. E. Brackett and W. F. Giauque, *ibid.*, **78**, 5747 (1956).

TABLE II

THERMODYNAMIC FUNCTIONS FOR H_2SO_4

0°C. = 273.15°K. gibbs mole^{-1} (see footnote 4a)

T	C_p	S	$-\left(\frac{F - H_0^0}{T}\right)$	$\left(\frac{H - H_0^0}{T}\right)$
15	0.78	0.269	0.083	0.186
20	1.64	0.607	.171	.436
25	2.56	1.071	.304	.767
30	3.46	1.616	.476	1.140
35	4.34	2.216	.681	1.535
40	5.16	2.850	.912	1.938
45	5.90	3.501	1.163	2.338
50	6.56	4.157	1.429	2.728
60	7.72	5.458	1.992	3.466
70	8.67	6.722	2.576	4.146
80	9.40	7.929	3.171	4.758
90	10.10	9.076	3.764	5.312
100	10.79	10.176	4.350	5.826
110	11.48	11.237	4.928	6.309
120	12.17	12.266	5.496	6.770
130	12.86	13.268	6.056	7.212
140	13.55	14.246	6.606	7.640
150	14.23	15.204	7.147	8.057
160	14.91	16.144	7.680	8.464
170	15.59	17.069	8.205	8.864
180	16.26	17.979	8.722	9.257
190	16.93	18.877	9.233	9.644
200	17.59	19.762	9.737	10.025
210	18.26	20.636	10.235	10.401
220	18.93	21.501	10.728	10.773
230	19.59	22.357	11.215	11.142
240	20.26	23.205	11.697	11.508
250	20.92	24.046	12.174	11.872
260	21.59	24.879	12.646	12.233
270	22.26	25.706	13.114	12.592
280	22.93	26.528	13.579	12.949
283.46(s)	23.16	26.812	13.739	13.073
283.46(l)	32.45	35.843	13.739	22.104
290	32.79	36.587	14.245	22.342
298.15	33.20	37.501	14.868	22.633
300	33.29	37.707	15.009	22.698

TABLE III

THERMODYNAMIC FUNCTIONS FOR $H_2SO_4 \cdot H_2O$

0°C. = 273.15°K. gibbs mole^{-1} (see footnote 16)

T	C_p	S	$-\left(\frac{F - H_0^0}{T}\right)$	$\left(\frac{H - H_0^0}{T}\right)$
15	0.56	0.190	0.063	0.127
20	1.27	.445	.124	.321
25	2.11	.816	.222	.594
30	3.02	1.282	.361	.921
35	4.01	1.822	.531	1.291
40	4.96	2.418	.729	1.689
45	5.79	3.049	.950	2.099
50	6.63	3.702	1.193	2.509
60	8.23	5.056	1.722	3.334
70	9.61	6.431	2.296	4.135
80	10.81	7.794	2.898	4.896
90	11.91	9.131	3.517	5.614
100	12.96	10.441	4.144	6.297
110	13.98	11.723	4.776	6.947
120	14.96	12.982	5.408	7.574
130	15.90	14.217	6.037	8.180
140	16.80	15.429	6.665	8.764
150	17.70	16.618	7.290	9.328
160	18.60	17.789	7.909	9.880
170	19.50	18.944	8.525	10.419
180	20.40	20.083	9.135	10.948
190	21.31	21.211	9.742	11.469
200	22.21	22.327	10.344	11.983
210	23.12	23.433	10.940	12.493
220	24.03	24.529	11.533	12.996
230	24.94	25.618	12.122	13.496
240	25.85	26.699	12.707	13.992
250	26.76	27.772	13.288	14.484
260	27.66	28.840	13.865	14.975
270	28.57	29.900	14.440	15.460
280	29.48	30.956	15.011	15.945
281.63(s)	29.63	31.128	15.104	16.024
281.63(l)	50.66	47.647	15.104	32.543
290	51.01	49.136	16.065	33.071
298.15	51.35	50.555	16.989	33.566
300	51.43	50.873	17.197	33.676

water and anhydrous sulfuric acid will be used as components of reference.

The values of the partial molal heat contents and partial molal heat capacities, with some data on the temperature coefficients of the partial molal heat capacities, are derived from the work of Kunzler and Giauque[6] and some results on the heat capacity of the more dilute solutions from Randall

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(4a) The most convenient way to tabulate the basic data of chemical thermodynamics, when it extends over a wide range of temperature, is in terms of the well known quantities $(F - H_0^0)/T$, $(H - H_0^0)/T$, S and C_p. Despite the very large amount of such data already accumulated, these tabulations are only beginning. The units practically always used for all of the above quantities are the defined cal. (°K.)$^{-1}$ for an amount of one g. mole. In the case of entropy this unit is sometimes referred to as the entropy unit, e.u., for brevity. This is not a satisfactory solution to the over-all problem because e.u. is not distinctive and in any case cannot properly be used for heat capacity or the other properties. Moreover, despite the basic nature of the entropy function, the primary motivation which has led to the tabulation of the above quantities is not entropy but the utility of the $(F - H_0^0)/T$ function in chemistry.

It was not necessary to define the unit known as the watt since we could use the term volt ampere, nor is the ohm essential since we could speak of volts ampere^{-1}; however, we doubt if any one could be found who would deny the utility of the terms watt and ohm. It seems to us to be at least of equal importance to have a name for a unit of such wide application as the cal. deg.$^{-1}$.

It seems desirable to have a name for this unit which is not associated specifically with F/T, H/T, S or C_p but which will apply to all of them, just as cal. (°K.)$^{-1}$ now does. Short monosyllabic names are best for units; Volta lost the a and it will not be long ere amp replaces ampere completely. In the present case the name Gibbs qualifies as concise and very deserving of the particular honor. Thus we have here used

$$1 \text{ gibbs} = 1 \text{ gbs.} = 1 \text{ defined cal. } (°\text{K.})^{-1}$$

and express hope that others will adopt this convenient abbreviation.

We are opposed to the use of joules rather than defined calories because the joule is defined in terms of basic electrical units and thus its energy value will continue to change slightly in terms of practical references. If a defined joule were adopted, it would soon involve a factor near unity between it and the absolute joule and one would never be sure whether such a factor had been used to divide or multiply. The factor 4.1840 absolute joules per defined calorie may be altered as absolute values of units are made more accurate, but it would be hard to misuse a factor of this magnitude.

For those who wish to use the B.t.u. and related units, it seems inevitable that considerations of convenience will lead to the use of a defined B.t.u. to match the defined calorie. Despite the importance of water, the dominating influence of the steam table will wane when it becomes just one more table, a process which is well under way. With such a defined B.t.u., and a Rankine absolute temperature scale anchored on the ice point alone, in order to be consistent with the similarly anchored Kelvin thermodynamic scale, recently adopted by international agreement, we have

$$1 \text{ gibbs mole}^{-1} = 1 \text{ defined cal. (deg. K.)}^{-1}(\text{g. mole})^{-1}$$
$$= 1 \text{ defined B.t.u. (deg. R)}^{-1}(\text{lb. mole})^{-1}$$

The convenience of having tables of $(F - H_0^0)/T$, $(H - H_0^0)/T$, S and C_p which would have identical entries for the two sets of units in common use should have wide appeal.

(5) J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 3472 (1952).

TABLE IV

THERMODYNAMIC FUNCTIONS FOR $H_2SO_4 \cdot 2H_2O$

0°C. = 273.15°K. gibbs mole^{-1} (see footnote 16)

T	C_p	S	$-\left(\frac{F - H_0^0}{T}\right)$	$\left(\frac{H - H_0^0}{T}\right)$
15	1.03	0.363	0.093	0.270
20	2.17	0.810	.211	0.599
25	3.32	1.419	.389	1.030
30	4.42	2.122	.617	1.505
35	5.51	2.886	.885	2.001
40	6.52	3.690	1.185	2.505
45	7.48	4.513	1.509	3.004
50	8.40	5.348	1.851	3.497
60	10.15	7.036	2.573	4.463
70	11.73	8.723	3.331	5.392
80	13.17	10.386	4.109	6.277
90	14.51	12.015	4.897	7.118
100	15.81	13.611	5.688	7.923
110	17.06	15.176	6.479	8.697
120	18.26	16.713	7.268	9.445
130	19.41	18.220	8.052	10.168
140	20.53	19.700	8.832	10.868
150	21.63	21.154	9.604	11.550
160	22.72	22.586	10.371	12.215
170	23.82	23.996	11.131	12.865
180	24.92	25.388	11.885	13.503
190	26.01	26.764	12.631	14.133
200	27.11	28.126	13.372	14.754
210	28.21	29.477	14.107	15.370
220	29.31	30.815	14.838	15.977
230	30.41	32.142	15.559	16.583
233.68(s)	30.81	32.629	15.827	16.802
233.68(l)	59.38	51.289	15.827	35.462
240	59.59	52.877	16.782	36.095
250	59.95	55.317	18.275	37.042
260	60.35	57.675	19.745	37.930
270	60.81	59.962	21.192	38.770
280	61.30	62.182	22.617	39.565
290	61.84	64.342	24.019	40.323
298.15	62.34	66.063	25.144	40.919
300	62.46	66.449	25.398	41.051

TABLE V

THERMODYNAMIC FUNCTIONS FOR $H_2SO_4 \cdot 3H_2O$

0°C. = 273.15°K. gibbs mole^{-1} (see footnote 16)

T	C_p	S	$-\left(\frac{F - H_0^0}{T}\right)$	$\left(\frac{H - H_0^0}{T}\right)$
15	1.14	0.398	0.101	0.297
20	2.37	0.890	.233	0.657
25	3.73	1.564	.429	1.135
30	5.08	2.364	.683	1.681
35	6.39	3.245	.986	2.259
40	7.67	4.182	1.326	2.856
45	8.91	5.157	1.697	3.460
50	10.12	6.158	2.093	4.065
60	12.43	8.209	2.941	5.268
70	14.58	10.290	3.842	6.448
80	16.46	12.363	4.778	7.585
90	18.16	14.400	5.734	8.666
100	19.77	16.397	6.701	9.696
110	21.33	18.355	7.672	10.683
120	22.84	20.276	8.642	11.634
130	24.31	22.162	9.610	12.552
140	25.76	24.017	10.573	13.444
150	27.20	25.843	11.530	14.313
160	28.65	27.645	12.481	15.164
170	30.13	29.426	13.426	16.000
180	31.64	31.190	14.364	16.826
190	33.18	32.942	15.295	17.647
200	34.75	34.684	16.221	18.463
210	36.32	36.417	17.142	19.275
220	37.91	38.143	18.057	20.086
230	39.50	39.863	18.968	20.895
236.76(s)	40.57	41.023	19.581	21.442
236.76(l)	74.29	65.251	19.581	45.670
240	74.35	66.261	20.204	46.057
250	74.54	69.300	22.108	47.192
260	74.77	72.228	23.979	48.249
270	75.04	75.055	25.819	49.236
280	75.39	77.790	27.627	50.163
290	75.81	80.442	29.402	51.040
298.15	76.23	82.549	30.826	51.723
300	76.32	83.021	31.147	51.874

and Taylor.[6] The heat capacity data on pure sulfuric acid and its several hydrates mentioned above also supply valuable information concerning the temperature coefficients of heat capacity of these liquids at their respective concentrations. At values of $A < 1.8$ we made some use of the data summarized by Socolik[7] in obtaining temperature coefficients.

The free energy of dilution requires the use of different experimental methods in various concentration ranges. Hornung and Giauque[8] measured the partial pressure of water over aqueous sulfuric acid at several temperatures above, as well as at, 25°, for $A = 2, 3$ and 4. At values of A greater than 2.5 there are excellent vapor pressure measurements of Shankman and Gordon,[9] who have summarized the earlier work of others, and at $A > 8$ there are measurements by Stokes.[10] At concentrations between $A = 2$ and the anhydrous acid there were essentially no activity data. For this reason Kunzler and Giauque[11] made accurate measurements of the freezing point over this region.

The thermodynamic properties of sulfuric acid and its mono-, di-, tri-, tetra- and hemihexahydrates are given in Tables II, III, IV, V, VI and VII.

The partial molal free energies over the range $A = -0.005$ to $A = 2$ made use of the computations made by Giauque, Kunzler and Hornung[12] who gave the variation over limited ranges. These computations were based on the freezing point curves mentioned above and the calorimetric data presented here. In order to refer the partial molal free energy of water to pure water as a standard state, the results for $A < 2$ are anchored on the vapor pressure measurements of Hornung and Giauque[8] at $A = 2$.

The unit of energy is the defined calorie = 4.1840 abs. joules. The gas constant $R = 1.98726$ cal. deg.$^{-1}$ mole^{-1}. This constant and all data have been corrected to the temperature scale, 0°C. = 273.15°K. (triple point of water = 273.16°K. exactly), in accordance with the recent international agreement. Since all of the low temperature heat capacity data on the hydrates of sulfuric acid have utilized the thermodynamic temperature scale of this Laboratory, which has been based only on an assumed ice point of 0°C. = 273.16°K., the correction requires only that the heat capacity data be multiplied by 273.16/273.15, and the temperatures multiplied by 273.15/273.16. This has been done. The molecular weight of water is taken as 18.016 and that of sulfuric acid as 98.082.

Heat of Dilution and Heat Capacity Data at 25°.—A recheck of the dilution data of Kunzler and Giauque[5] in connection with the preparation of the final smoothed thermodynamic properties of aqueous sulfuric acid showed small discontinuities between their series 1, 2, 3 and 4. It was possible to trace the error to the way in which the samples

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(6) M. Randall and M. D. Taylor, *J. Phys. Chem.*, **45**, 959 (1941).

(7) S. Socolik, *Z. physik. Chem.*, **A158**, 305 (1932).

(8) E. W. Hornung and W. F. Giauque, THIS JOURNAL, **77**, 2744 (1955).

(9) F. Shankman and A. R. Gordon, *ibid.*, **61**, 2370 (1939).

(10) R. H. Stokes, *ibid.*, **69**, 1291 (1947).

(11) J. E. Kunzler and W. F. Giauque, *ibid.*, **74**, 5271 (1952).

(12) W. F. Giauque, J. E. Kunzler and E. W. Hornung, *ibid.*, **78**, 5482 (1956).

TABLE VI

THERMODYNAMIC FUNCTIONS FOR $H_2SO_4 \cdot 4H_2O$

0°C. = 273.15°K. gibbs mole^{-1} (see footnote 16)

T	C_p	S	$-\left(\frac{F - H_0^0}{T}\right)$	$\left(\frac{H - H_0^0}{T}\right)$
15	1.87	0.687	0.179	0.508
20	3.50	1.445	.395	1.050
25	5.27	2.415	.699	1.716
30	7.02	3.532	1.077	2.455
35	8.67	4.739	1.513	3.226
40	10.24	6.001	1.995	4.006
45	11.74	7.293	2.512	4.781
50	13.20	8.606	3.055	5.551
60	15.79	11.247	4.200	7.047
70	18.06	13.855	5.394	8.461
80	20.03	16.399	6.611	9.788
90	21.83	18.863	7.836	11.027
100	23.51	21.252	9.060	12.192
110	25.14	23.570	10.274	13.296
120	26.73	25.827	11.477	14.350
130	28.32	28.031	12.666	15.365
140	29.92	30.187	13.840	16.347
150	31.52	32.305	15.002	17.303
160	33.13	34.391	16.148	18.243
170	34.75	36.448	17.282	19.166
180	36.39	38.482	18.404	20.078
190	38.03	40.493	19.514	20.979
200	39.69	42.487	20.612	21.875
210	41.35	44.464	21.702	22.762
220	43.03	46.426	22.781	23.645
230	44.72	48.377	23.851	24.526
240	46.42	50.316	24.915	25.401
244.88(s)	47.25	51.261	25.431	25.830
244.88(l)	89.96	81.169	25.431	55.738
250	90.16	83.028	26.589	56.439
260	90.57	86.573	28.829	57.744
270	91.00	89.999	31.032	58.967
280	91.46	93.317	33.197	60.120
290	91.94	96.534	35.327	51.207
298.15	91.35	99.091	37.037	62.054
300	92.44	99 660	37.419	62 241

TABLE VII

THERMODYNAMIC FUNCTIONS FOR $H_2SO_4 \cdot 6.5H_2O$

0°C. = 273.15°K. gibbs mole^{-1} (see footnote 16)

T	C_p	S	$-\left(\frac{F - H_0^0}{T}\right)$	$\left(\frac{H - H_0^0}{T}\right)$
15	2.04	0.721	0.136	0.585
20	4.06	1.579	.310	1.269
25	6.33	2.723	.673	2.050
30	8.65	4.083	1.126	2.957
35	9.14	5.587	1.654	3 933
40	13.06	7.185	2.245	4.940
45	15.10	8.841	2.885	5.956
50	17.04	10.533	3.566	6.967
60	20.83	13.979	5.013	8.966
70	24.45	17.463	6.543	10.920
80	27.62	20.946	8.125	12.821
90	30.09	24.344	9.740	14.604
100	32.64	27.644	11.366	16.278
110	35.18	30.874	12.992	17.882
120	37.65	34.041	14.615	19.426
130	40.09	37.150	16.229	20.921
140	42.52	40.211	17.834	22.377
150	44.97	43.228	19.426	23.802
160	47.41	46.208	21.007	25.201
170	49.89	49.157	22.576	26.581
180	52.37	52.078	24.134	27.944
190	54.85	54.975	25.681	29.294
200	57.34	57.852	27.218	30.634
210	59.82	60.709	28.744	31.965
220	62.31	63.550	30.262	33 288
220.27(s)	62.39	63.626	30.303	33.323
220.27(l)	124.59	100.646	30.303	70.343
230	127.04	106.085	33.395	72.690
240	129.36	111.542	36.538	75.004
250	131.31	116.863	39.645	77.218
260	132.91	122.045	42.714	79.331
270	134.19	127.086	45.746	81.340
280	135.15	131.985	48.740	83.245
290	135.86	136.740	51.692	85.048
298.15	136.30	140.512	54.069	86.443
300	136.38	141.356	54.605	86.751

taken during these measurements, and put aside, were handled before analysis. Since the weights of all amounts of stock solution and water added to the calorimeter were accurately known, together with the analysis of the stock solution, all data were recalculated on this basis. This removed the discontinuities and also led to slightly improved thermodynamic consistency in several respects. In addition several other small errors were eliminated.

The corrections to the above work may be outlined as follows: Their "Table III," "Series 1": The 2nd to 5th and the 26th values of A_{av} should be altered to 0.2454, 0.2889, 0.3329, 0.3757 and 1.3817. After this correction is made, add (0.0098 + 0.00215A) to *all* of the A_{av} values in the series. The 2nd to 5th values of ΔA should be altered to 0.04231, 0.04473, 0.04321 and 0.04256. After this correction is made, add 0.00215 ΔA to *all* values of ΔA. All $\bar{L}_1$ values are correct. "Series 2" may be corrected to a sufficient accuracy by adding 0.00490 to each A_{av} value. ΔA and $\bar{L}_1$ are unchanged. "Series 3": 13th and 14th A_{av} should be changed to 0.1994 and 0.2365. Then add 0.00192 to *all* A_{av} values in the series. ΔA is unchanged. The 1st to 4th, 6th, 7th and 13th values of $\bar{L}_{1av}$ should be changed to 943, 947, 942, 927, 695, 541 and 415.9. "Series 4": The 1st, 2nd and 5th values of $\bar{L}_{1av}$ should be changed to 92.94, 78.56 and 35.74, respectively. "Series 5": The 3rd A_{av} value should be 31.398.

"Table V," Heat Capacity. "Series 1": Multiply all values of wt. % by 0.9982. "Series 2": Multiply the first eight values of wt. % by 0.9991 and the last two values by 0.9998. "Series 3": Multiply all values of wt. % by 0.9998.

It was necessary to apply a small correction to the heat capacity data of Randall and Taylor[6] in order to express their results in defined calories. Essentially their results are proportional to an assumed heat capacity of water taken as 17.976 cal. deg.$^{-1}$ mole^{-1} at 25°. De Haas[13] has prepared a table for converting such earlier results. This table is quoted by Stimson.[14] At 25°,

$$C_p = 4.1793 \text{ absolute joules deg.}^{-1}\text{ g.}^{-1}$$
$$= \frac{4.1793 \times 18.016}{4.1840}$$
$$= 17.996 \text{ defined cal. deg.}^{-1}\text{ mole}^{-1}$$

and thus the results of Randall and Taylor were multiplied by the factor 1.7996/1.7976 = 1.00111.

The free energy, heat of dilution, entropy and heat capacity data are given in Table I.

$$\bar{L}_1 = \left(\frac{\partial L}{\partial n_1}\right)_{n_2} \text{ and } \bar{C}_{p_1} = \left(\frac{\partial C_p}{\partial n_1}\right)_{n_2}$$

where n_1 and n_2 refer to the number of moles of H_2O and H_2SO_4, respectively. Pure H_2O and pure H_2SO_4 are used as standard states of reference.

The heat of dilution calorimeter utilized by Kunzler and Giauque[5] was designed for use in the more concentrated solutions and was quite unsuitable in very dilute solutions.

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(13) W. J. de Haas, *Procès-Verbaux Comité International Poids et Mesures*, **22**, 92 (1950).

(14) H. F. Stimson, *Amer. J. Phys.*, **23**, 614 (1955).

Fortunately Young, Groenier and Wu[15] have been investigating the very dilute solutions with calorimeters which give high accuracy in this region. During the course of these researches the two groups have exchanged data. The $\bar{L}$ values have been joined smoothly in the region about $A = 20$. Thus the values given in our table for $A > 20$ are taken from the work of Young, Groenier and Wu.

The values of the partial molal entropies $\bar{S}_1$ and $\bar{S}_2$ do not include the contributions due to the nuclear spin of hydrogen and are thus the ones which should be used in ordinary thermodynamic calculations. The absolute values can be obtained by adding $R \ln 4$ to $\bar{S}_1$ and to $\bar{S}_2$. The entropy effect due to isotopes is neglected as is customary and in this case happens to be negligible.

Figure 1 shows the freezing point curves for all known phases in the sulfuric acid–water system.

Correlation of the Entropies Obtained from the Third Law of Thermodynamics with the Data at 298.15°K.—As we have mentioned above, the low temperature data on all of the hydrates showed agreement with the third law of thermodynamics within the small limits of experimental error. The collected results are presented in Table VIII. In order to test the data, the entropy of H_2SO_4 was assumed to be correct. This and the accurately known entropy of liquid water, 16.71 cal. deg.$^{-1}$ mole^{-1}, and the isothermal entropy changes, $(\Delta H - \Delta F)/T$, were used to calculate the entropy values for the several hydrates.

TABLE VIII

ENTROPIES OF SULFURIC ACID HYDRATES AT 298.15°K.

Gibbs mole^{-1} (see footnote 16)

Substance	$\int_0^T C_p \, d \ln T$	Using $(\Delta H - \Delta F)/T$
H_2O	(16.71)	
H_2SO_4	(37.50)	
$H_2SO_4 \cdot H_2O$	50.49	50.56
$H_2SO_4 \cdot 2H_2O$	66.04	66.06
$H_2SO_4 \cdot 3H_2O$	82.55	82.55
$H_2SO_4 \cdot 4H_2O$	99.07	99.09
$H_2SO_4 \cdot 6.5H_2O$	140.61	140.51
$H_2SO_4 \cdot 8H_2O$	....	165.46

It is evident that the data on all of the measured hydrates agree very well. None of the hydrates has crystalline disorder at limiting low temperatures. The values in Table VIII were based on the original observations. The values in Tables II to VII inclusive have been adjusted by small amounts, well within the limits of accuracy, so that all of the tables of thermodynamic data are made internally self-consistent.

The Activities in Aqueous Sulfuric Acid.—The activity coefficient γ of sulfuric acid and the activity of water are given in Table IX. All of the data in the tables given above are in terms of pure H_2SO_4 as the standard state. However in Table IX the activity coefficient of H_2SO_4 is given in terms of the more usual hypothetically molal solution as unit activity since many will prefer this convention. The value of γ has been anchored on $\gamma = (0.130)$ for $m = 1$. This value has been taken from Harned and Owen.[16] Any later change in this value will affect all γ values in direct proportion.

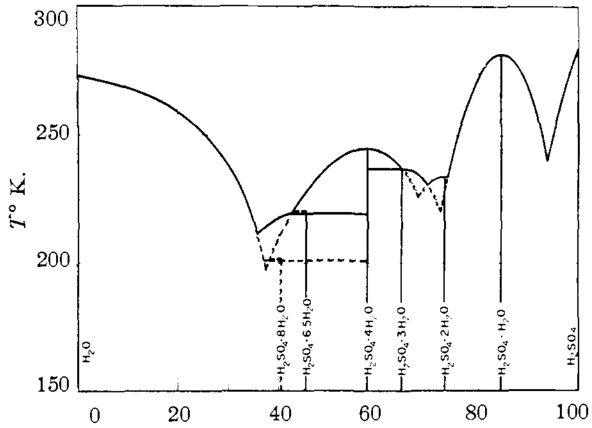

Fig. 1.—Freezing point curves for H_2SO_4–H_2O.

Glueckauf and Kitt[18] recently have measured the activities of water by an isopiestic method involving the use of concentrated sulfuric acid solu-

TABLE IX

ACTIVITY COEFFICIENT OF SULFURIC ACID AND THE ACTIVITY OF WATER IN AQUEOUS SULFURIC ACID AT 298.15°K.

m	γ	$a_\omega = p/p^0$
1	(0.130)	9.622×10^{-1}
2	.1253	9.130×10^{-1}
3	.1411	8.514×10^{-1}
4	.1683	7.800×10^{-1}
5	.2062	7.035×10^{-1}
6	.254	6.257×10^{-1}
7	.315	5.503×10^{-1}
8	.385	4.806×10^{-1}
9	.464	$4\ 175 \times 10^{-1}$
10	.555	3.611×10^{-1}
11	.656	3.113×10^{-1}
12	.766	2.678×10^{-1}
13	.884	2.303×10^{-1}
14	1.010	1.980×10^{-1}
15	1.143	1.701×10^{-1}
16	1.286	1.462×10^{-1}
17	1.435	1.255×10^{-1}
18	1.593	1.077×10^{-1}
19	1.761	9.233×10^{-2}
20	1.932	7.929×10^{-2}
25	2.842	3.799×10^{-2}
30	3.736	1.937×10^{-2}
35	4.557	1.042×10^{-2}
40	5.28	5.90×10^{-3}
45	5.88	3.53×10^{-3}
50	6.33	2.23×10^{-3}
60	6.81	1.05×10^{-3}
70	6.91	5.80×10^{-4}
80	6.80	3.61×10^{-4}
90	6.57	2.47×10^{-4}
100	6.30	1.79×10^{-4}
200	3.98	3.20×10^{-5}
300	2.83	1.38×10^{-5}
400	2.19	7.87×10^{-6}
500	1.78	5.20×10^{-6}
1000	0.92	1.50×10^{-6}
∞	0^a	1.56×10^{-9}

^{a} $a_2(m = \infty) = 3.41 \times 10^9$.

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[15] T. F. Young, W. L. Groenier and Y. C. Wu (private communication).

[17] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 576.

[18] E. Glueckauf and G. P. Kitt, *Trans. Faraday Soc.*, **52**, 1074 (1956).

tions at 0.4 and 25°. They estimate the accuracy of their determinations of the activity of water at about 1% above $m = 30$. Comparing their smooth table with the present results, Glueckauf and Kitt are lower by 1.3% at $m = 30$, 2.8% at $m = 40$, 1.3% at $m = 50$ and 3.6% at $m = 60$. They also give a result at $m = 70$ which is 7.3% low; however this appears to be extrapolated since the highest observation in a table of the actual observations kindly supplied to us by the authors was 66.73 molal. Aside from the 3.6% difference at $m = 60$, which occurs near the limit of the isopiestic method, the agreement is very satisfactory.

The Stability of the Low Temperature Phases in the H_2SO_4–H_2O System.—Ordinarily the temperature regions of stability of the various possible phases in a system are obtained by direct observation. This becomes increasingly impracticable due to decreasing rate of transition as temperature is lowered. In the present case data are available to obtain this information by calculation. One may inquire concerning such possibilities as

$$2H_2SO_4\cdot3H_2O = H_2SO_4\cdot4H_2O + H_2SO_4\cdot2H_2O$$

or

$$7H_2SO_4\cdot4H_2O = 2H_2SO_4\cdot6.5H_2O + 5H_2SO_4\cdot3H_2O$$

The free energy change in all such possible reactions was found to be positive at all temperatures down to 0°K. Thus no intermediate hydrate becomes unstable with respect to a higher and a lower hydrate. The calculations are straightforward and need not be discussed here. The possibility of a hydrate becoming unstable with respect to ice and a lower hydrate was also investigated. This case presents some calculation difficulties, since ice has residual entropy due to disordered hydrogen bonding at low temperatures; however, it is possible to conclude that none of the hydrates up to the hemihexa becomes unstable with respect to splitting out ice at low temperatures.

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BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY AND THE GENERAL ELECTRIC RESEARCH LABORATORY]

An Analysis of Polymorphism in Boron Based upon X-Ray Diffraction Results[1]

BY J. L. HOARD AND ARTHUR E. NEWKIRK

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X-Ray powder diffraction patterns are computed from single crystal data for tetragonal and β-rhombohedral boron. Critical examination of reported powder data from more than a dozen boron samples shows that (1) β-rhombohedral boron is generally to be expected from high temperature preparation with or without fusion, (2) besides the three established modifications, there are several other claimants to recognition. This multiplication of structural variants apparently is dictated by kinetic factors. It is suggested that boron prepared by deposition onto heated substrates is especially prone to form monotropes, often as non-stoichiometric borides.

Introduction

The definite characterization of three crystalline modifications of elemental boron has been in each case an immediate consequence of success in growing single crystals of these polymorphs.[2-4] More usually, the products obtained from boron-rich systems have been notably diverse microcrystalline aggregates, giving X-ray powder diffraction patterns which have defied simple interpretation. Such difficulties need no longer be exaggerated through lack of authoritative patterns for the established polymorphs. The powder diagram for (low temperature) *α-rhombohedral* boron has been published[5]; the patterns for *tetragonal*[2,6] boron and (high temperature) *β-rhombohedral*[3] boron, computed from spectrometrically measured single crystal data, are given in Tables I and II of this paper. When powder diffraction data from various preparations of boron, old and new, are examined in the light of the established patterns, the following general conclusions emerge.

The complex patterns have only too frequently been recorded at very low resolution on a heavy and rapidly varying background, to give spacings for low scattering angle sometimes not reliable to better than two significant figures. While use of accurate spacings from the single crystal data permits some allowance for apparently systematic trends in the reported values, the identification of phases achieved in these circumstances must be recognized as probable rather than certain. The advantages of recording with chromium Kα radiation, the longest generally practicable wave length, become so manifest that the line intensities of Tables I and II are given for this case.

Some powder diagrams from fairly pure boron samples indicate the existence of other polymorphs. We note specifically the recently obtained evidence for a second *tetragonal*[7] modification: namely, the successful indexing in terms of a very large cell (*ca.* 192 atoms) of some 50 lines from the diffractometer trace given by an apparently quite

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[1] Supported in part by a National Science Foundation Grant to Cornell University.

[2] A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

[3] D. E. Sands and J. L. Hoard, *ibid.*, **79**, 5582 (1957).

[4] L. V. McCarty, J. S. Kasper, F. N. Horn, B. F. Decker and A. E. Newkirk, *ibid.*, **80**, 2592 (1958).

[5] B. F. Decker and J. S. Kasper, *Acta Cryst.*, **12**, 503 (1959).

[6] J. L. Hoard, R. E. Hughes and D. E. Sands, THIS JOURNAL, **80**, 4507 (1958); *cf.* J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

[7] B. Post, private communication, 1959.