Heat Capacities for the Water–Hydrogen Peroxide System between 25° and 60° C.

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CALORIMETRIC measurements were made before on mixtures of hydrogen peroxide and water over the whole concentration range at 0° C. in an ice calorimeter (*1*) and at 26.9° C. in an isothermal diphenyl ether calorimeter (*3*). From these earlier data it was possible to derive the thermodynamic excess functions in that temperature range (*4*). Because the catalytic decomposition of hydrogen peroxide increases rapidly on warming, measurements at higher temperatures are difficult and subject to serious errors. Scatchard and coworkers (*7*) have used their results on the vapor pressure of hydrogen peroxide–water mixtures at 60°, 75°, and 90° C. to calculate a number of related properties by an empirically fitted equation for the free energy changes. Because the coefficients in their equation were smoothed for temperature, comparison of the properties derived therefrom with our own calorimetric data for 26.9° C. was not warranted. On the other hand, extrapolation of the latter much above 25° was also uncertain in view of the irregular behavior of the excess functions at lower temperatures, specially for the more dilute solutions. [Cf. (*4*), Figure 6.].

This work reports on the direct determination of the average heat capacities for these binary mixtures over two temperature ranges up to 60° C.

EXPERIMENTAL PROCEDURE

Measurements were carried out by the drop method with the isothermal calorimeter previously described (*2*). The calibration factor found by Jessup (*6*), 18.90 cal./gram Hg, was used instead of the former one, 19.01 (*2*), although the difference between the two was generally within the present experimental errors. The samples were brought into thermal equilibrium at 45° or 60° in an all-glass water jacket (*1*) the temperature of which was kept constant to within ±0.01° and measured on a precision mercury-in-glass thermometer calibrated against a Leeds and Northrup platinum resistance thermometer. The samples were prepared and analyzed as described before.

Occasionally the calorimeter yielded some erratic results which could easily be spotted as they were much in error (and always too low). This occured mostly after a number of determinations had been made with the same mantle of solid diphenyl ether. This behavior, unobserved previously, must be a consequence of the method followed—sudden

Table I. Average Heat Capacities of H_2O-H_2O_2 Solutions

Concn. 100 w_p[a]	Wt. of Soln., G.	ΔH Measured, Cal.	C_p, Cal./Deg. G.
	(Between 26.9° and 45° C.)		
0	1.0405	18.800	0.9983
5.4	1.0502	18.840	0.9722
10.2	1.0287	17.584	0.9444
17.2	1.6384	27.128	0.9148
31.4	1.4642	22.887	0.8636
52.2	1.5032	21.499	0.7902
71.2	1.2309	16.175	0.7260
89.2	2.0247	24.381	0.6653
	(Between 26.9° and 60° C.)		
0	0.6690	22.117	0.9988
4.4	0.7910	23.032	0.9678
15.6	0.8051	24.623	0.9240
26.7	0.9249	27.136	0.8864
49.2	0.9798	26.113	0.8052
70.1	1.0027	24.341	0.7334
92.4	1.2030	26.089	0.6552

[a] Weight per cent of H_2O_2.

Table II. Smoothed Values of Heat Capacities and Related Properties of H_2O-H_2O_2 Mixtures

$100\ N_p$ = mole fraction of H_2O_2.
$\overline{C}_p$ = average heat capacity.
$\Delta\overline{C}_p = (1+n)\,\overline{C}_p(\text{solution}) - n\overline{C}_p(H_2O\ \text{l.}) - \overline{C}_p(H_2O_2\ \text{l.})$.
$\theta\overline{C}_p = (1+n)\,\overline{C}_p(\text{solution}) - (1+n)\,\overline{C}_p(H_2O\ \text{l.}) - \frac{1}{2}\,\overline{C}_p(O_2\text{g.})$.
$n = N_w/N_p$.

Comp.		Mol. Wt.	$\overline{C}_p$ Cal./Deg. G.		Cal./Deg. Mole H_2O_2			
					$\Delta\overline{C}_p$		$\theta\overline{C}_p$	
100 w_p	100 N_p		[a]	[b]	[a]	[b]	[a]	[b]
0	0	18.02	0.998	0.998_5	...	...	...	...
10	0.056	18.92	0.945	0.946	−4.82	−5.00	5.00	5.00
20	0.117	19.89	0.904_5	0.908_5	−3.25	−2.74	3.42	2.82
30	0.185	20.98	0.869_5	0.873_5	−1.89	−1.57	2.11	1.68
40	0.261	22.20	0.835	0.838	−1.18	−1.00	1.34	1.11
50	0.346	23.56	0.800_5	0.803_5	−0.78	−0.69	0.95	0.78
60	0.443	25.11	0.765_5	0.769	−0.52	−0.43	0.70	0.54
70	0.553	26.86	0.731_5	0.733_5	−0.31	−0.31	0.47	0.42
80	0.679	28.88	0.696	0.698_5	−0.19	−0.18	0.35	0.28
90	0.827	31.25	0.661_5	0.663	−0.07	−0.07	0.24	0.18
100	1.00	34.02	0.626_5	0.628_5	0.0	0.0	0.16	0.10

[a] Average values between 25° and 45° C. [b] Average values between 25° and 60° C.

Table III. Smoothed Values of the Heat of Mixing and the Heat of Vaporization for H_2O-H_2O_2 Mixtures

Concn.	$-\Delta H_M$ (Cal./Mole H_2O_2)						$\Delta H_{\text{vap.}}$ (Cal./G. Soln.)			
100 w_p	0°	25°	45°	60°	75°	Ref. (7)	0°	25°	45°	60°
0	590[a]	815[a]	950[a]	1030[a]	1110[a]	1110[a]	596.0	582.1	571.2	563.2
10	640	807	907	986	1045	1036	576.1	563.4	552.9	545.4
20	667	787	856	888	900	949	556.0	543.5	533.4	526.4
30	667	753	793	803	820	870	535.3	523.8	514.3	507.1
40	641	704	729	741	750	778	51.41	503.1	494.1	487.4
50	594	637	654	663	670	682	492.8	482.2	473.7	467.3
60	515	545	556	561	565	570	470.3	460.4	452.0	446.0
70	417	436	443	447	450	450	447.5	437.8	430.0	424.1
80	295	306	310	313	315	316	423.5	414.1	406.5	401.3
90	157	162	163	164	165	166	397.8	388.8	383.1	376.6
100	0	0	0	0	0	0	370.9	362.7	356.3	351.3

[a] Extrapolated.

addition of a fairly large amount of heat—coupled with the low thermal conductivity of the solid ether. Holmberg (*5*) pointed out that the diphenyl ether calorimeter gives better results when the heat is supplied slowly. The practice was adopted thereafter of preparing a new mantle after 3 or 4 runs.

EXPERIMENTAL RESULTS

The numbers in Table I represent a typical set of results. From a large scale plot of these the smoothed values given in Table II were obtained. The same symbols and presentation (*3*) are used here. With these new data it is now possible to calculate as a function of temperature up to 60° and above various thermodynamic properties of hydrogen peroxide–water mixtures with better accuracy. For convenience the heat of vaporization and the integral heat of solution of hydrogen peroxide as a function of concentration are shown in Table III. The values of the latter at 75° were extrapolated from the present measurements for comparison with the qunatities derived by Scatchard and coworkers (*7*) from vapor pressure measurements. Agreement between the two is excellent except in the 20 to 30% concentration range. Excess entropy and free energy functions are listed in Table IV for 0°, 25°, and 75° C.

ACKNOWLEDGMENT

The authors are grateful to the Shell Oil Co. of Canada for a fellowship granted to J.L. Carmichael.

Table IV. Thermodynamic Excess Functions of H_2O-H_2O_2 Mixtures

Concn.	$-\Delta F^E$ (Cal./Mole)			$T\Delta S^E$ (Cal./Mole)		
100 w_p	0°	25°	75°	0°	25°	75°
0	0	0	0	0	0	0
10	44	43	38	−8	3	20
20	83	79	72	−5	13	33
30	125	117	110	−2	22	42
40	153	144	137	14	40	58
50	176	166	159	30	54	73
60	187	178	170	41	63	80
70	183	176	167	48	65	81
80	155	150	141	45	57	73
90	97	92	86	33	42	50
100	0	0	0	0	0	0

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RECEIVED for review January 31, 1962. Accepted May 17, 1962.