to 95 tons of coal per day. In spite of the widely different local conditions of the three laboratories there is no evidence that variations in season or proximity of large consumers of fuel cause any measurable differences in carbon dioxide and oxygen content of the atmospheric air. As pointed out by Benedict,[2] many of the atomic weights are not known beyond the fourth significant figure, but here is a physical mixture of gases, with the percentage content of one of its constituents, namely oxygen, having a constancy beyond the accuracy of many atomic weight determinations.

The analyses were made at Durham by Mrs. H. H. Latimer and Mr. N. F. Colovos, at Baltimore by Mr. K. Koudelka, and at Boston by Mr. E. L. Fox.[5]

Summary

Three series of samples of outdoor air consisting of 75 at Durham, New Hampshire, 790 at Baltimore and 291 at Boston were analyzed for carbon dioxide and oxygen content by means of an apparatus on which readings are estimated to 0.001%. Each series was scattered over nearly the same number of days as there were analyses. The grand average of all three series gave 0.031% for carbon dioxide and 20.939% for oxygen. In spite of widely different local conditions of the three laboratories there was no evidence that variations in season or proximity of large consumers of fuel caused any measurable differences in carbon dioxide and oxygen content of atmospheric air.

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[5] Died Dec. 19, 1934.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Note on the Relative Partial Molal Heat Content of Zinc Sulfate in Aqueous Solution

BY HERBERT S. HARNED

Cowperthwaite and La Mer[1] have measured the electromotive forces of the cells

Zn(2-phase amalgam) | $ZnSO_4(m)$ | $PbSO_4$-Pb(2-phase amalgam)

at concentrations from 0.0005 to 0.01 M, and from 0 to 50° at 12.5° intervals. They showed that these results were in conformity with the Gronwall, La Mer and Sandved[2] extension of the Debye and Hückel theory, provided that 3.64 Å. was used for the mean distance of approach of the ions, a. With this equation, they obtained the standard potentials of the cell at the temperatures at which they were measured.

From these data, La Mer and Cowperthwaite[3] have computed the relative partial molal heat content, $\bar{L}_2$. This quantity has also been obtained from calorimetric data by Lange, Monheim, and Robinson,[4] who derived values which differed considerably from those computed from the electromotive forces. Such a discrepancy detracts from the value of Cowperthwaite and La Mer's proof of the validity of the extended theory unless it can be shown that this disagreement disappears upon further consideration of the results.

Following Cowperthwaite and La Mer, we shall employ the quantity E_0', defined by the equation of the cell by

$$E_0' = E + \frac{\gamma RT}{NF}\ln m = E_0 - \frac{\gamma RT}{NF}\ln \gamma \qquad (1)$$

where E is the measured electromotive force corrected for lead sulfate solubility, E_0 the standard potential of the cell, and the other symbols have their usual connotation. The calculation of $\bar{L}_2$ by La Mer and Cowperthwaite is open to two criticisms. In the first place, they employed a five constant power series equation ending in a term containing T^4 to express five results. If one or more of the results are in error, this procedure will not yield an accurate temperature coefficient at a given temperature. Secondly, their results at 50° were obtained with difficulty and in fact seem to be inconsistent with the results at the lower temperatures. Electromotive force measurements as a function of temperature usually may be expressed with high accuracy by a quadratic equation. To test this in the present instance, the first order differences of Cowperthwaite and La Mer's results[1] were plotted against T. These plots are straight lines with the exception of the one which involves the 50° reading, a fact which indicates that a quadratic equation may

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[1] Cowperthwaite and La Mer, THIS JOURNAL, 53, 4333 (1931).

[2] Gronwall, La Mer and Sandved, *Physik. Z.*, 29, 358 (1928).

[3] La Mer and Cowperthwaite, THIS JOURNAL, 55, 1004 (1933).

[4] Lange, Monheim and Robinson, *ibid.*, 55, 4733 (1933).

be used to compute E'_0 from 0 to 37.5°. In Table I are given the constants of the equations

$$E' = E'_{25} + a'(t - 25) + b'(t - 25)^2 \qquad (2)$$

and

$$E_0 = E_{0(25)} + a'(t - 25) + b'(t - 25)^2 \qquad (3)$$

where E_0 is the standard potential. These equations will express the results with an average deviation of 0.07 mv. in regions of concentration from 0.001 to 0.01 M, inclusive. The 0.0005 M result is not so good, but the values of E_0 from the extrapolation of Cowperthwaite and La Mer agree with those computed by equation (3) to within 0.05 mv. On the absolute temperature scale these equations become

$$E'_0 = a + bT + cT^2 \qquad (4)$$

$$E_0 = a_0 + b_0T + c_0T^2 \qquad (5)$$

from which $\bar{L}_2$ in calories may be computed as shown by Harned and Thomas[5] by

$$\bar{L}_2 = -46{,}118\ [(a - a_0) - (c - c_0)T^2] \qquad (6)$$

The values of a were smoothed by plotting against m. In Table I, values of $(a - a_0)$, $(c - c_0)$ and $\bar{L}_2$ computed by this method are collected. In the eighth column are given the values of this quantity calculated by Lange, Monheim and Robinson from their heat of dilution data. The agreement between the values derived from these two types of measurement is good, particularly since an error of 0.001 mv. per degree in the temperature coefficient of electromotive force causes an error of 14 cal. in $\bar{L}_2$. Further, since an error of 0.1 in the estimation of $(c - c_0) \times 10^7$ produces an error of 41 cal., the discrepancy at 0.0005 M is not serious. Indeed, it is hardly likely under the most favorable circumstances that $\bar{L}_2$ can be estimated from these results with an accuracy greater than 30 cal. In the last column of the table the results of La Mer and Cowperthwaite's calculation are given. As the concentration increases, there is an increasing deviation between their results and those derived from heat of dilution data which amounts to 200 cal. at 0.01 M. At 0.0005 M, La Mer and Cowperthwaite's value checks the calorimetric, but as previously mentioned this may not be significant since the whole computation is so sensitive and since the electromotive force data are less consistent at this concentration.

TABLE I

$\bar{L}_2$ OF ZINC SULFATE. CONSTANTS OF EQUATIONS (2), (3) AND (6)

m	$E_{0(25)}$	$(-a'_0 \times 10^3)$	$(-b'_0 \times 10^6)$					
0.0	0.41087	1.106	4.00	....		...	...	...
	E'_{25}	$(-a' \times 10^3)$	$(-b' \times 10^6)$	$(a - a_0)$	$(c - c_0) \times 10^7$	$\bar{L}_2$, e. m. f.	$\bar{L}_2$, cal.	$\bar{L}_2$ La M.
0.0005	0.41725	1.085	3.93	0.0019	0.7	(198)	255	266
.001	.42002	1.052	3.87	.0032	1.3	385	355	395
.002	.42365	1.025	3.82	.0055	1.8	480	492	563
.005	.42989	1.005	3.76	.01024	2.4	674	676	812
.01	.43524	0.980	3.68	.01525	3.2	772	790	978

Summary

By employing a quadratic equation to express the electromotive force data of the cell[1] Zn (2-phase amalgam) | $ZnSO_4(m)$ | $PbSO_4$-Pb (2-phase amalgam) from 0 to 37.5° with the omission of an uncertain result at 50°, values of the relative partial molal heat content of zinc sulfate were computed. These values are in agreement with those obtained by measurements of heats of dilution,[4] a fact which seems to justify our method of procedure. We may conclude that from 0 to 37.5° the electromotive force data possess a high accuracy which we judge to be of the order of ±0.05 mv. If the method here employed is correct, the previous discrepancy between the values of $\bar{L}_2$ obtained from heat data[4] and electromotive force measurements[3] disappears. This agreement is excellent evidence for Cowperthwaite and La Mer's extrapolation of the electromotive forces, and lends confirmation to their proof of the effect of the extended terms of the Debye and Hückel theory.

NEW HAVEN, CONN.

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(5) Harned and Thomas, THIS JOURNAL, 58, 761 (1936).