iron have been made. Since such measurements will, it is hoped, be made in this Laboratory at a later date, calculations of the free energy of these substances will be deferred.

Although the data for the oxides of copper are of sufficient accuracy to permit calculations of their free energies, their consideration is most profitable in connection with the measurements of the e.m.f. of cells reported in the paper by Maier.[10]

Summary

The heat capacities of "ferrous oxide" and of cuprous and cupric oxide have been measured from 70 to 300°K., and of magnetite from 60 to 300°K.

Their entropies are:

	FeO	Fe_3O_4	Cu_2O	CuO
S°_{298}	12.7 ± 2.0	34.69 ± 0.2	21.7 ± 1.0	9.75 ± 0.05

BERKELEY, CALIFORNIA

NOTES

A Simple Apparatus for the Determination of Carbon Dioxide.—The following method has been worked out for the accurate determination of carbon dioxide in limestone. The originality, we believe, lies in the simplification of the apparatus and in the arrangement to minimize contamination with atmospheric carbon dioxide.

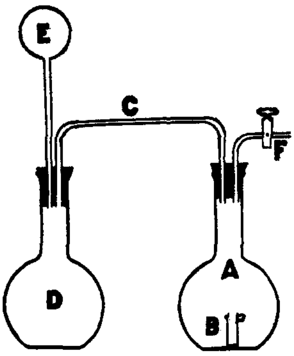

Fig. 1.

No special apparatus is required; two ordinary 1-liter Pyrex flasks, a small rubber balloon, two rubber stoppers and some large glass tubing are all that is necessary.

Chromic acid is used to liberate the carbon dioxide, and this is absorbed in a carefully standardized solution of barium hydroxide. The excess barium hydroxide is then titrated with standard hydrochloric acid, using phenolphthalein as indicator.

Procedure.—Set up the apparatus as shown in the figure and make sure that it is air tight. Weigh out 0.1000 g. of carbonate into B, place 100 cc. of a 1% aqueous solution of chromic anhydride in A and 50 cc. of water in D. Heat the contents of both A and D to boiling, remove both flames and add 25 cc. of a 0.2 *N* barium hydroxide solution to D. Carefully lower the bottle B containing the charge into A with a copper wire without letting the acid come in contact with the carbonate. Quickly stopper both A and D, which are thus connected by the tube C. Shake flask A to overturn B, place D in cold water and boil the contents of A. The balloon E serves as a safety valve, pressure regulator and pressure indicator. After boiling for about thirty minutes, remove the flame from beneath A and admit carbon dioxide-free air through F. The flask D should be now at about room temperature. Disconnect it and titrate the excess barium hydroxide with standard hydrochloric acid, using phenolphthalein as indicator.

The advantages of the method are that no train is necessary and the apparatus is cheap and easy to set up. It is likewise easy to clean. The results obtained are quite accurate. In the case of pure calcium carbonate 44.08 and 43.93 instead of 44.00% were obtained. With sodium carbonate the results were likewise accurate.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND
R. C. WILEY

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Note on the Determination of the Activity of One Substance from that of Another by a Cell with a Liquid Junction.—In connection with work done in this Laboratory it was desired to know the activity coefficient of perchloric acid over a range of concentrations. On investigation of the literature, an article by Schuhmann[1] was found in which he states that the activity coefficient of perchloric acid is the same as that of hydrochloric acid of the same molality, at all concentrations up to 1.1 molal. His conclusions are based upon measurements of the cell H_2, $HCl(c)$, $HClO_4(c)$, H_2, since he obtains electromotive forces which are the same as those given by the Lewis and Sargent formula for this kind of liquid junction.

MacInnes and Yeh[2] have given a simple and reasonable derivation of this formula. When the cell operates, certain dilutions and concentrations will occur with respect to Cl^- and ClO_4^- in the composition gradient portion of the cell. (This composition gradient was of course set up by diffusion.) These effects are accompanied by the free-energy changes always involved in diluting or concentrating a substance. The "liquid potential" is the summation of these free energies, in joules per coulomb, when the cell operates reversibly. When the cell operates in a given direction, the relative speeds of Cl^- and ClO_4^- during current flow determine the extent to which the dilutions outweigh the concentrations, or the reverse, and this in turn determines the magnitude and sign of the "liquid potential," since dilution occurs with a decrease and concentration with an increase in free energy. MacInnes and Yeh derive the Lewis and Sargent formula, which involves the ion mobilities, by employing the ordinary equation for the free energy of dilution, assuming that the mobility and activity coefficient of each ion are constant over the entire gradient,

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[1] Schuhmann, THIS JOURNAL, **46**, 58 (1924).

[2] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

but not that the activity coefficients of all the ions are the same. They assume also a constant composition gradient. The assumption of a constant activity coefficient for a given ion is in accordance with experiment and with the well-known "principle of the ionic strength" of Lewis and Randall and the Debye-Hückel interionic attraction theory. They integrate the free energies of changes in concentration from a point beyond which no Cl^- ever enters to a point beyond which no ClO_4^- ever enters (using the above case as an example). The only reaction in the above cell not accounted for by these assumptions is the formation and disappearance of H^+ at the electrodes and its transport through the cell. If Schuhmann obtains the electromotive force given by the Lewis and Sargent formula, the formation and transport of H^+ must occur with no free-energy change. What these experiments seem to prove, then, is that the activity of H^+ in HCl solutions is the same as that of H^+ in $HClO_4$ solutions of the same molality, but not that the activity of Cl^- in aqueous HCl is the same as that of ClO_4^- in aqueous $HClO_4$ of the same molality. The experiments, therefore, do not prove that the mean activity of the ions, or the activity coefficient of the electrolyte, is the same for HCl and $HClO_4$ of the same molality. In fact, the use of mean activities is a mathematical device to avoid the use of individual ion activities, and is only exact for reactions which can be written in molecular form without arbitrary assignment of positive ions to negative ions, that is, reactions for which the product of the ion activities occurs in the equation connecting free energy with concentration. Practically all the cells used in activity determinations have been such as to involve the formation of the given compound from substances other than ions.

It is possible, of course, that Cl^- and ClO_4^-, because of the symmetrical electronic structure of both these ions, have the same activities in equimolal solutions of the two acids, up to 1.1 molal. Their mobilities are, in fact, nearly the same. It should be noted, however, that the individual ion activity of ClO_3^- is noticeably less than that of Cl^- in solutions of the same ionic strength, according to the table of Lewis and Randall. Other experiments of this type, or the determination of the activity of perchloric acid by freezing-point methods, might prove enlightening. Possibly the method could be used for the determination of individual ion activities. Meanwhile it is felt, in view of the above considerations, that the method used by Schuhmann is not evidence for equal mean activity coefficients in equimolal solutions of two electrolytes with a common ion.

Contribution from the
Chemical Laboratory of the
University of Nebraska

Ralph F. Nielsen
Herman A. Liebhafsky

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