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# Heat of Solution of Liquid Bromine in 2*M* NaOH at 27° C.

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**The heat of solution of liquid $Br_2$ in excess 2.0*M* NaOH has been measured in a diphenyl ether, change-of-phase calorimeter at 27° C. and found to be 10.3 ± 0.2 kcal. per mole of $Br_2$.**

THE TWO RECENT DETERMINATIONS of the heat of solution of liquid $Br_2$ in aqueous NaOH at 25° C. differ by about 5%. Although this difference does not significantly affect values for the thermochemical functions of the hypohalites it is interesting that in one research, done at relatively high NaOH concentrations (0.25 to 1.3*M*) (*4*), no dependence of heat of solution on NaOH concentration was noted, while in the other work (*3*), the heat of solution was observed to increase with increasing NaOH concentration in the range 0.025 to 0.1*M*.

We have used the reaction between liquid $Br_2$ and excess 2.0*M* NaOH to evaluate the performance of a Bunsen or change-of-phase calorimeter when the reactants are mixed by the up-and-down motion of a hand-operated Teflon disk affixed to a glass breaker. The results are reproducible to within the limits of precision indicated by the calibration constant and agree with the extrapolated value at infinite NaOH dilution obtained by McDonald and Cobble (*3*), 10.35 ± 0.20 kcal. per mole at 25° C.

## EXPERIMENTAL AND DISCUSSION

The construction and calibration of the diphenyl ether calorimeter have been described (*1*). The present instrument was calibrated both by electrical heating and by using the standard reaction between 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris or Tham) and 0.1*N* HCl, for which enthalpies have been measured (*2*). The result of four electrical calibrations was 0.348 ± 0.01 cal. per cm. and for eight Tham calibrations was 0.337 ± 0.01 cal. per cm. These results agree within the limits of their precision. However, since the rate of heat evolution during Tham calibrations was similar to the rate of heat evolution during hydrolysis experiments, the Tham calibration factor was used in calculating heats from the mercury thread extension in the dilatometer tube of the calorimeter.

Table I. Heat of Solution of Liquid Bromine in 2.0*M* NaOH at 27° C.

| $Br_2$, Mmoles | $OBr^-$, Mmoles | Measured Exothermic Heat, Cal. | Kcal./Mole $Br_2$ |
|---|---|---|---|
| 1.008 | 1.00 | 10.4 | 10.3 |
| 2.884 | . . . | 29.0 | 10.1 |
| 1.678 | 1.69 | 18.3 | 10.9 |
| 5.320 | 5.22 | 53.9 | 10.1 |
| 3.390 | 3.39 | 35.7 | 10.5 |
| 2.859 | 2.80 | 28.6 | 9.99 |
| 3.702 | . . . | 38.2 | 10.3 |
| 2.620 | 2.62 | 27.8 | 10.6 |
| 3.316 | 3.30 | 34.1 | 10.3 |
| | | | Av. 10.3 ± 0.2 |

Analar analytical grade bromine was weighed and sealed into thin-walled glass bulbs which were broken and stirred into 25.0 ml. of 2.0*M* NaOH in a reaction tube placed in the calorimeter. A heat of breaking and stirring was determined in blank experiments (0.56 ± 0.18 cal., exothermic) and subtracted from all heat of solution experiments.

Following the heat determination, if any unreacted $Br_2$ could be seen in the reaction mixture the experimental result was discarded. In almost all experiments the reaction mixture was analyzed iodometrically for hypobromite ion. The results are given in Table I.

The yield of hypobromite is variable and on the average about 0.7% below that demanded by the stoichiometry:

$$Br_2(liq) + 2NaOH(aq) = NaBr(aq) + NaOBr(aq) + H_2O$$

A similar result was found by McDonald and Cobble

(3) and Wu, Birky, and Hepler (4). Disproportionation of hypobromite to bromate occurs slowly at the temperature of the experiments. In this work, however, because of the limited accuracy of the calorimetric results, no correction to the $-\Delta H$ values for hypobromite loss was made.

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# Solubility of Carbon Dioxide in Pure Water, Synthetic Sea Water, and Synthetic Sea Water Concentrates at −5° to 25° C. and 10- to 45-Atm. Pressure

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**Experimental equipment and procedure are described for measuring high pressure, low temperature solubility of gases in liquids. Experimental results are given for the solubility of $CO_2$ in distilled water, synthetic sea water, and synthetic sea water concentrates in the −5° to 25° C., 10- to 45-atm. range.**

IN 1960 the Jacobs Engineering Co., Pasadena, Calif., under contract to the State of California, Department of Water Resources, issued a report (*7*) of a preliminary engineering study of its proposed process for saline water demineralization. This process, a freezing, or alternatively a hydrate process, proposed the use of carbon dioxide as a direct contact refrigerant or hydrating agent. The report pointed out the dearth of reliable experimental data on the solubility of carbon dioxide in liquids of interest, sea water and sea water concentrates produced by the freezing of pure ice from sea water.

The university agreed to undertake an experimental program to supply the necessary data. It was originally believed that this work would be relatively routine; that this did not prove to be the case has been chronicled in the annual report (*17, 18*) and most recently the final project report (*19*) of the university's Sea Water Conversion Laboratory, which is based upon Munjal's thesis (*12*).

Prior work in this field can be conveniently divided into the solubility of carbon dioxide in water and in salt solutions.

The solubility of carbon dioxide in water has been investigated by numerous workers from the time of Wrobleski (*23, 24, 25*) in 1882. The data in the literature have been compiled by several writers (*13, 14, 16*), the most recent of whom are Dodds, Stutzman, and Sollami (*4*), who covered the information available through 1955. Since then the works of Bartholome and Friz (*1*) and Loparest (*9*) have appeared. The agreement among the results of the various investigators is by no means as good as is desirable, particularly in the higher pressure region. Hydrate formation in this higher pressure area, delineated by Larson (*8*) who worked out the phase diagram for the $CO_2$—$H_2O$ system, may well account for at least some of the disagreement.

The solubility of $CO_2$ in solutions of various inorganic salts [NaCl, $NaNO_3$, $Na_2SO_4$, $KNO_3$, $Mg(NO_3)_2$, and $MgSO_4$] at 1-atm. pressure is summarized by Markham and Kobe (*11*) in their literature survey. Findlay and Creighton (*5*) investigated KCl solutions.

Surprisingly enough, especially considering the importance of carbon dioxide in the biological field, apparently no experimental measurements have been made on the solubility of $CO_2$ in sea water. Quoted values for this property are usually taken from Buch (*3*); these tables were based on Bohr's (*2*) estimate that the gas solubility was the same in sea water as in a NaCl solution containing the same quantity of dissolved solids. Lyman (*10*) has examined this assumption, and concludes that Buch's values are slightly high.

A much more complete review of prior work, including many tables, is given by Munjal (*12*) and in the project report (*19*).

## EXPERIMENTAL EQUIPMENT

From a functional point of view the equipment used in the experimental work served two purposes: to prepare a sample at equilibrium at a known pressure and temperature, and to ascertain the composition of that sample. The components or subsystems of the equi-

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