Solubility and Heat of Solution of Carbon Dioxide in Aqueous Solutions of Arsenous Oxide, Arsenic Pentoxide, and Hydrochloric Acid

Standard State Correction for the Combustion Calorimetry of Organochlorine Compounds

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The solubility of CO_2 in aqueous solutions of As_2O_3, As_2O_5, and HCl was determined from 20° to 30° C. by the gas volumetric method. This information is needed for the calculation of the correction to "standard states" in the combustion calorimetry of organic compounds containing chlorine. The apparatus and procedure, which allows the preparation of solutions of known concentration in gas-free water in situ, are described.

THE heats of combustion and formation of organochlorine compounds can be determined with considerable accuracy by combustion calorimetry using a platinum lined rotating bomb calorimeter. The calculation of the values from the measured energy of the bomb reaction includes corrections to the standard states for all reaction products. Since the combustion of chlorine compounds in an oxygen atmosphere generally produces some free chlorine gas as well as hydrochloric acid, it is customary to add an aqueous solution of As_2O_3 to the bomb to reduce the Cl_2 to HCl. The corrections to be considered in the calculations, then, include a consideration of the heat liberated by the solution of carbon dioxide in the resulting bomb solution, which contained As_2O_5, HCl, and unreacted As_2O_3. However, the quantity and the molar heat of solution of CO_2 dissolved in the final solution has not been determinable. Therefore, it has been necessary to incorporate the correction in the calibration of the bomb by running a comparison experiment for each run on the unknown compound. The comparison experiment involves making up a solution of identical composition as the final bomb solution in the test run and then making a calibration run using a known sample, such as benzoic acid and diethyl oxalate, in a ratio which will reproduce the heat and the amount of CO_2 liberated in the test run. This obviously involves a great deal of extra experimental work and increases the chance of error, since only one calibration run is generally used for each calculation instead of an average of several runs. The purpose of this paper was to provide the data necessary to allow the direct calculation of the correction for the solution of CO_2 and eliminate the need of the extra comparison experiments.

EXPERIMENTAL

Materials. WATER. Conductivity water was prepared as described by Barber, Handley, and Herington (*1*). The water was then distilled from a quartz still and stored in a quartz flask until used. The water used had a specific conductance of less than 1×10^{-7} reciprocal ohm.

As_2O_3, As_2O_5. Fisher Certified Reagents, purity better than 99.3%.

Apparatus and Procedure. The general arrangement of the apparatus used in this study is shown in Figure 1. The CO_2 was purified in the line and sublimed into the system since, although the manufacturer reported a purity of 99.9%, there were small amounts of noncondensable gases present. Mercury levels were read with a cathetometer to ± 0.05 mm. Atmospheric pressures were read to ±0.1 mm. with a mercury barometer and were corrected to 0° C. The bath temperature was controlled to ±0.05° C. and was measured with a National Bureau of Standards certified thermometer. The room temperature was held sufficiently constant and uniform to avoid any significant errors from temperature fluctuations.

Since the room temperature and/or the barometric pressure may change during a measurement, the volume of

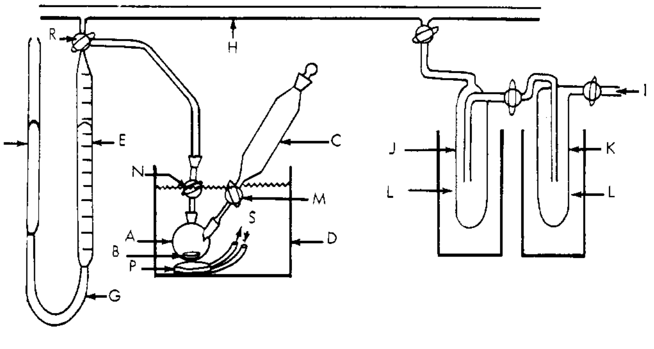

Figure 1. CO_2 absorption apparatus

A. Reaction flask, 2-necked, approx. 50 ml.
B. Magnetic stirring bar
C. Addition funnel
D. Constant temperature bath
E. Mercury gas buret, 100 ml.
F. Leveling tube
G. Plastic connecting tube
H. High vacuum line
I. CO_2 inlet (connected to tank of compressed, purified CO_2)
J. Trap
K. Trap
L. Liquid nitrogen Dewar flasks
M. Stopcock
N. Stopcock-adaptor
P. Immersible magnetic stirrer
R. 3-way stopcock
S. To water line

the buret and connection from the zero graduation (top mark) of the buret to stopcock N must be known. This can be determined as follows: Stopcock N is closed. Dry air (or CO_2) is admitted to the buret, and stopcock R is closed to the line, H, open to E and N. The volume is read on the buret, and the pressure is determined from the barometric pressure and the mercury levels. The pressure is then changed by raising or lowering the leveling tube, F, and the volume and mercury levels are again read. Several sets of readings are taken, and the volume from the zero mark to N is then calculated from the ideal gas laws. This volume must always be added to the volume read on the buret.

The volume of the reaction flask is determined with the funnel, C, and the stopcock-adaptor, N, in place by weighing it empty and filled with water at a known temperature (stopcock M closed). The volumes thus determined were reproducible to ±0.02 ml.

The addition funnel is evacuated and the reaction flask is filled with "conductivity" water (*1*) or a solution of purified HCl in water. The water (or solution) is fully degassed by boiling under reduced pressure and the funnel is filled and weighed. The reaction flask is dried and the solid As_2O_3 and/or As_2O_5 is weighed in. The apparatus is assembled and the buret and flask are evacuated. Stopcock N is closed and the water-HCl is added from the funnel. Stopcock M is closed and the stirrer started. Heating is usually necessary to hasten solution of the As_2O_3–As_2O_5. Pure, gas-free water is distilled into trap J, and CO_2 is condensed in trap K. Any noncondensable gases are pumped off. Trap J is then warmed and a small amount of water vapor is condensed in the buret by slightly cooling the walls. This is to ensure saturation of the gas with water vapor. CO_2 is then allowed to sublime into the buret and tube to stopcock N. The three way stopcock R is then closed to the vacuum line and, with mercury levels in E and F approximately even, the volume, mercury levels, temperature, and barometric pressure are read. Stopcock N is then opened. Stirring is continued during absorption and the leveling tube, F, is raised to maintain atmospheric pressure. When no further absorption occurs, the volume, mercury levels, temperature, barometric pressure, and water bath temperature are read. (Complete saturation is usually attained in about 4 or 5 hours, but the absorption was generally allowed to continue overnight.) The addition funnel is removed and reweighed. The vapor pressure of the solution may be taken from the literature, determined separately, or, at temperatures above the ambient, the stopcock N may be opened and the pressure read by the mercury levels before water vapor is admitted to the buret. The amount of HCl added may be determined by titrating the solution remaining in the funnel. The density of the solution is determined with a calibrated pycnometer.

Calculations. The heat of solution of CO_2 in the given solutions can be calculated from the experimental data by the following equation:

$$\ln \frac{\alpha_1}{\alpha_2} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

where ΔH is the differential heat of solution of 1 mole of the gas in a saturated solution and α_1 and α_2 are the Bunsen adsorption coefficients at temperatures T_1 and T_2, respectively. The Bunsen absorption coefficient, α, which is defined as the volume of gas reduced to standard conditions (0° C. and 760 mm.) dissolved in one volume of water when the pressure of the gas (without the aqueous tension) is 760 mm., is calculated by the following formula (*6*):

$$\alpha = \frac{273\left\{\frac{y(P - f)}{T} - \frac{z(P_1 - f_1)}{T_1} - \frac{x(P_1 - f_2)}{T_2}\right\}}{V(P_1 - f_2)} \qquad (2)$$

where:

V = volume of solvent
x = volume of gas and vapor in flask at end = (volume of flask) − (volume of solution)
y = volume of gas in buret at start
T = temperature at start, ° K.
P = pressure of gas at start, mm.
f = aqueous vapor pressure at temperature T
z = volume of gas in buret at end
T_1 = temperature at end, ° K.
P_1 = pressure of gas at end, mm.
f_1 = aqueous vapor pressure at temperature T_1
T_2 = temperature of sample, ° K.
f_2 = vapor pressure of sample at temperature T_2

The partial pressure of the CO_2 in the combustion bomb can readily be calculated and the value of the absorption coefficient at that pressure (generally more than 760 mm. of Hg) can be determined from Henry's Law, stated as:

$$m = kP \qquad (3)$$

where m is the mass of gas, P is the pressure, and k is a constant, assuming that it is valid over the pressure range used. Experimental evidence in this work at pressures from 300 to 840 mm. of Hg revealed no discrepancies.

The Bunsen absorption coefficients can be converted to values of Henry's law constants in mole liter^{-1} atm.$^{-1}$ by dividing by 22.26—this factor contains an allowance for the departure of carbon dioxide from the ideal gas law.

As a general rule, if only the salting-out effect of the solute is considered, the variation of gas solubility with the concentration of the solute species can be represented, at least approximately, by an equation of the form (*4*):

$$\log (S/S_0) = -kc \qquad (4)$$

where:

S = solubility of the gas in the solution
S_0 = solubility of the gas in pure water
k = constant
c = concentration of solute

The solubility of the gas in a solution with several different solutes can then be calculated by the equation:

$$\log S = \log S_0 - k_1c_1 - k_2c_2 - k_3c_3 - \cdots \qquad (5)$$

Accuracy of Measurements. The accuracy and reliability of the equipment and procedure were determined by measurements of the solubility of CO_2 in pure conductivity water. The average value of the Bunsen absorption coefficient determined for five runs was 0.758 at 25° C. with a range of ±1.1%. The literature value (*2*) is 0.759.

RESULTS

The solubility of CO_2 was determined in aqueous solutions of As_2O_3 and AS_2O_5 in the range of 0 to 0.12 molal and 0 to 0.15 molal, respectively. The limited solubility of the arsenic acids prevented the use of higher concentrations. (The acids were finely powered and required vigorous stirring at 90° C. for up to 5 hours to obtain complete solution.) The solubility of CO_2 in HCl solutions was determined from 0 to 10 molar HCl. The results are given in Table I.

The experimental data (up to approximately 1 molar in the case of HCl) fit the form of Equation 4 well. The values obtained for the constant, k, are given in Table II, with the solubilities given as the Bunsen absorption coefficient and the concentrations in molality (moles per 1000 grams of H_2O).

At the low concentrations of the As_2O_3 and As_2O_5 solutions used, the plots of the absorption coefficient for CO_2 *vs.* the concentration of the arsenic acid gave virtually straight

Table I. Solubility of CO_2 in Aqueous Solutions of As_2O_3, As_2O_5, HCl

Molality			α		
As_2O_3	As_2O_5	HCl	20° C.	25° C.	30° C.
. . .	. . .	. . .	. . .	. . .	0.743 (27.3°)
. . .	. . .	. . .	. . .	0.750	. . .
. . .	. . .	. . .	. . .	0.763	. . .
. . .	. . .	. . .	. . .	0.760	. . .
. . .	. . .	. . .	. . .	0.762	. . .
0.1113	. . .	. . .	0.835	0.724	0.633
0.1113	. . .	. . .	. . .	0.720	0.635
0.0649	. . .	. . .	0.855	0.735	0.651
0.0344	. . .	. . .	0.880	0.749	0.662
. . .	0.0262	. . .	0.866	0.756	0.663
. . .	0.0509	. . .	0.865	0.748	0.655
. . .	0.1330	. . .	0.841	0.737	0.640
0.0329	0.0273	. . .	0.864	0.744	0.649
. . .	. . .	0.1866	. . .	0.752	. . .
. . .	. . .	0.6370	0.854	0.743	0.647
. . .	. . .	1.261	. . .	0.728	. . .
. . .	. . .	2.562	. . .	0.735	. . .
. . .	. . .	7.459	. . .	0.812	. . .
. . .	. . .	10.971	0.938	0.818	. . .
. . .	. . .	12.754	0.924	0.816	. . .
0.0305	0.0307	0.1271	1.029	0.789	0.653
0.0465	0.0159	0.0625	0.854	0.732	0.650
. . .	. . .	. . .	. . .	0.757	. . .

Table II. Salt-Effect Constants, Equation 5

Solute	*K*. 1000Grams of H_2O/Mole
As_2O_3	0.180
As_2O_5	0.129
HCl	0.015

lines (Figures 2 and 3). In the case of the solubility of CO_2 in solutions of HCl, which was carried to higher concentrations, a curve was obtained (Figure 4), for which Equation 4 holds approximately only until the minimum at about 1.5 molal HCl. Markham and Kobe (5) obtained similar curves for the solubility of CO_2 in sulfuric and perchloric acids solutions.

The straight line equations of solubility in 0 to 0.1 molal acid solutions were determined from Figures 2, 3, and 4, and are listed in Table III, where *S* is the solubility of CO_2 in the solution, S_0 is the solubility in pure water at the same temperature and pressure, and *C* is the acid concentration in molality.

One run was made with a mixture of As_2O_3 and As_2O_5 and two runs were made with mixtures of As_2O_3, As_2O_5,

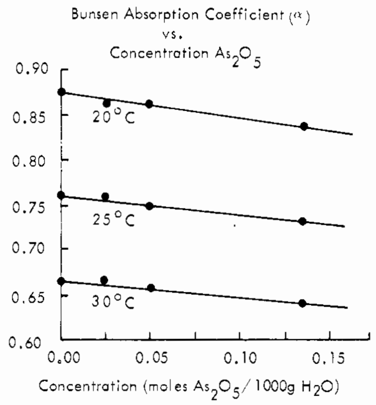

Figure 3. Solubility of CO_2 in aqueous As_2O_5

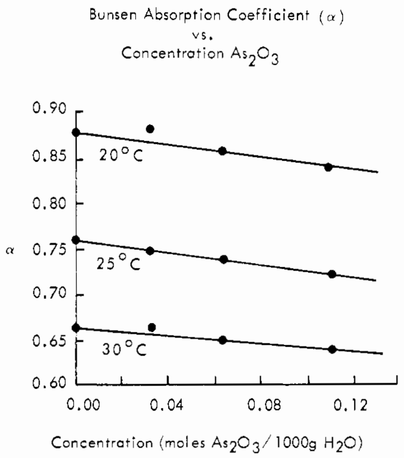

Figure 2. Solubility of CO_2 in aqueous As_2O_3

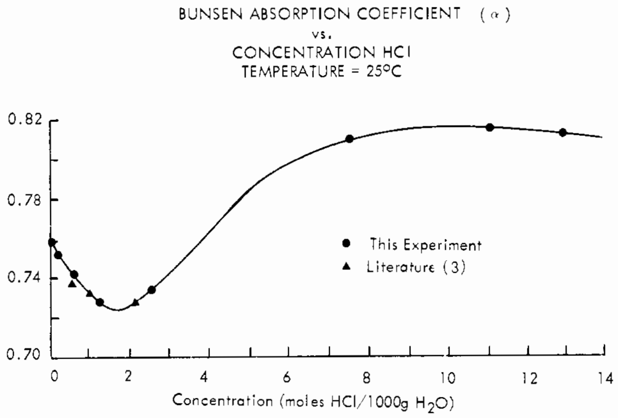

Figure 4. Solubility of CO_2 in aqueous HCl

and HCl in solution. The results agreed very well with the values calculated by Equation 5 (Table IV). The calculated results are nearly identical with those calculated by the equations in Table III.

The heats of solution of CO_2 in the various solutions were calculated by Equation 1 from the values of α at 20° and 30° C., assuming a relatively constant value of ΔH in that range. The results are listed in Table V.

Table III. Linear Solubility Relationships

$C = 0$ to 0.1 molal

Solution	CO_2 Solubility Equation
As_2O_3	$S = S_0(1 - 0.41C)$
As_2O_5	$S = S_0(1 - 0.29C)$
HCl	$S = S_0(1 - 0.04C)$

Table IV. Values Calculated by Equation 5

Molality			Temp., °C.	α	
As_2O_3	As_2O_5	HCl		Calcd.	Found
0.0329	0.0273	...	20	0.859	0.864
...	...	...	25	0.743	0.744
...	...	...	30	0.651	0.649
0.0465	0.0159	0.0625	20	0.855	0.854
...	...	...	25	0.739	0.732
...	...	...	30	0.648	0.650
0.0305	0.0307	0.1271	30	0.648	0.653

Table V. Calculated Values of $\Delta H_{\text{sol.}}$ CO_2

Solution	ΔH, Cal./Mole
Water	−4900
0.1113 molal As_2O_3	−4892
0.133 molal As_2O_5	−4822
0.637 molal HCl	−4890

DISCUSSION

The plots of the absorption coefficients *vs.* concentration of the acid species (Figures 2 and 3) at different temperatures have approximately equal slopes and can be represented by the same general equation (Table III) within experimental error. This would indicate that there is no appreciable change in the heat of solution of CO_2 per mole within the concentration ranges used. This fact is further illustrated by the data in Table V, where the calculated values of the heats of solution are equal within experimental error. Therefore, the authors concluded that the heat of solution of CO_2 per mole in any of the solutions generally encountered in calorimetric work ($< 0.1M$ As_2O_3) can be considered equal to that in pure water. The maximum error introduced by this assumption, calculated from the data in Table V and assuming the use of 20 ml. of a 0.1 molal As_2O_3 solution in the bomb, would be on the order of 0.2 calorie.

The change in solubility of CO_2 in solutions of up to 0.1 molal As_2O_3 is rather significant. The decrease in the amount of CO_2 dissolved in the bomb solution from that in pure water may be more than 5%. With 20 ml. of solution in the bomb, this would amount to an error of about 0.9 calorie. Therefore, it may be advantageous to compute the correction for the solubility of CO_2 in the final bomb solution considering the salting-out effect of the various species present. This calculation should also take into account the usual correction for the fugacity of CO_2 in the presence of oxygen.

LITERATURE CITED

(1) Barber, C.R., Handley, R., Herington, E.F.G., *Brit. J. Appl. Phys.* **5**, 41–4 (January 1954).
(2) Bohr, Chr., *Wied. Ann.* **68**, 504 (1899).
(3) Geffcken, Gustav, *Z. Physik. Chem.* **49**, 257 (1904).
(4) Glasstone, Samuel, "Text-book of Physical Chemistry," p. 689, Van Nostrand, New York, 1940.
(5) Markham, A.E., Kobe, K.A., *J. Am. Chem. Soc.* **63**, 1165–6 (1941).
(6) Reilly, J., Rae. W.N., "Physico-chemical Methods," Vol. **III**, p. 147, Van Nostrand, New York, 1948.

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Thermal Conductivity of Fibrous Silica

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The thermal conductivity of fibrous-silica high temperature insulation, commercially available as Dynaquartz, was measured in air, argon, and under high vacuum from 735° to 2860° R. mean temperature.

CRYSTALLINE fibrous-silica insulation, commercially available as Dynaquartz (*5*), has properties which make it a promising material for high temperature use. These are: a low density of 6.2 pounds per cubic foot (p.c.f.); good dimensional stability with less than 1.0% shrinkage after several hours at 3060° R.; maximum rated temperature of 3210° R.; and chemical stability characterized by low volability and low reactivity (*5, 7, 8, 11*).

The material used in this investigation was 99+% crystalline silica in randomly oriented fibrous form. The range of observed fiber diameter was 3.3 to 6 microns. The true density of the fibers was determined to be 2.17 grams per cc. The void volume fraction was 0.954. Figure 1 is a photomicrograph of the fibrous silica sample.

The thermal conductivity of fibrous silica insulation, obtained with a guarded hot plate apparatus, is reported.