Thermochimica Acta, 115 (1987) 67–81
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A MICROCALORIMETRIC METHOD FOR THE MEASUREMENT OF ENTHALPIES OF SOLUTION OF GASES IN LIQUIDS

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(Received 23 September 1986)

ABSTRACT

An experimental set-up for measuring enthalpies of solution of gases in liquids is described. This apparatus consists of a vacuum line for gas handling and a Tian–Calvet microcalorimeter. The gas quantities are measured by a mercury manometer. The gas is injected into the calorimeter cell through a sintered glass–mercury one-way valve.

The various sources of systematic and random errors are analyzed.

The experimental method allows the measurement of the reaction stoichiometry and the distinction between fast and slow reactions, on the calorimeter time-constant scale.

Along with spectroscopic studies of the reaction products, these features enable a more thorough characterization of the final state than the usual calorimetric techniques used for similar studies.

A summary of the applications in the fields of physical organic chemistry, polymer chemistry and natural gas refining is given.

INTRODUCTION

Solution calorimetry is applied to a wide range of chemical problems [1,2] but only a few works are devoted to solution of gases in liquids and still at present most of the reported enthalpies of gas–liquid reactions are obtained from variations of solubility with temperature [3]. This approach generally leads to data of significantly lower precision than calorimetry and is limited to measurements on low-solubility compounds. This situation is probably due to the fact that direct measurement of enthalpies of solution of a gas in a liquid involves hyphenated techniques, i.e. calorimetry (or microcalorimetry) coupled with gas-handling, which both are usually considered difficult by the scientific community. During the past 15 years our laboratories have been engaged in a systematic study of acid–base reactions using mainly a microcalorimetric method to measure enthalpies of reaction. The most used reference acid was pure, gaseous boron trifluoride. Although very hygroscopic and reactive, this Lewis acid proved to give very good results when

0040-6031/87/$03.50

manipulated in a vacuum line coupled to a calorimeter, as already observed by Brown et al. [4,5] with various gaseous boron compounds.

Our apparatus, including a Calvet heat-conduction microcalorimeter, is applicable to all reactions of the type:

$$\text{liquid} + \text{gas} \rightarrow \text{product(s)} + \text{heat} \qquad (1)$$

if the gas is condensable with liquid dinitrogen (LN_2) and if compounds are compatible with glass, valve materials (grease, PTFE, etc.) and mercury. The mercury gauge may be replaced by other manometers [6] (capacitance, high-precision Bourdon with SiO_2 tube or Wallace–Tiernan type, or even piezoelectric sensors) depending on price and performance requirements.

In the present paper we describe our experimental set-up and we give a report of its performance and reproducibility along with some examples of its uses in our laboratories.

TECHNICAL CHOICE

The initial aim of our experimental set-up was to measure the enthalpy of reaction between a gaseous Lewis acid (generally hygroscopic and corrosive) and a Lewis base as pure liquid or in solution in a non-reacting solvent. To handle such gases we have chosen to work in a vacuum line [4,7], the transfers being made by using LN_2 trapping and therefore our apparatus concerns condensable gases.

Several techniques for bringing the gases into the calorimeter are reported in the literature. The gas may be injected from a gas-tight syringe [8,9], or carried into the calorimeter by a stream of inert gas bubbling through a sample of the solute kept liquid with a bath at an appropriate temperature [10]. The gas can be delivered at a constant rate by an Hg piston, either into a bell immersed in the liquid [8,11] or through a thin-walled stainless-steel entry tube dipped into a cup of mercury located at the bottom of the vessel in order to prevent the backflow of solution up the gas entry tube [7]. The gas–liquid mixing was also obtained by raising a central receptacle, which dipped into a small pool of mercury providing a separation between the gas contained in the receptacle and the liquid contained in the outer vessel [12]. Steady-state flow calorimetry for the solution of gases slightly soluble in water was also used [13] and recently improved [14].

In our apparatus the gas is permitted to pass under its own pressure through a sintered glass disk covered with mercury, acting as an effective one-way valve [4]. Only a small differential pressure is necessary to overcome the mercury pressure over the valve (about 15 mm of mercury above the sintered glass disk are used to obtain a good seal); this overpressure is generated by a slow warming of the gas trapped at the LN_2 temperature.

The calorimeters generally used for gas–liquid reactions are "pseudo-adiabatic", Dewar-vessel-like, or more precisely, isoperibol [4,7,8], isothermal [9] or (strictly speaking) adiabatic [10]. Corollary few authors used heat-conduction calorimeters [13,14] and only one used a Tian–Calvet microcalorimeter [12]. We have also chosen this solution owing to the several advantages presented by this technique over "pseudo-adiabatic" calorimeters: smaller samples and/or higher sensitivity, very stable and reproducible baseline, high accuracy and repeatability when properly used, very high calibration stability and easy output handling by signal integration. We shall see later how this gives distinct advantages.

DESCRIPTION OF THE EXPERIMENTAL APPARATUS

Calorimeter

The Tian–Calvet calorimeter (built in the Centre de Thermodynamique et de Microcalorimétrie machine shop at Marseille) has two cells (reference and sample) of 17 mm diameter. Each calorimetric element contains 128 chromel–constantan thermocouples. By means of a switching arrangement the number of thermocouples in the detecting circuit can be reduced to 64. The working temperature range is 278–423 K (similar calorimeters are built by Setaram). The highest sensitivity is 45 μV mW^{-1} and the time constant τ is 240 s. ($\tau = t_{1/2}/\ln 2$, $t_{1/2}$ being the time required for the thermal decay curve to fall to half of its value in the steady-state condition [15,16]. τ may also be defined [17] as one-sixth of the settling time, where the settling time is the time required to reach 99.75% of the final steady state after an instantaneous pulse of heat. In these conditions $\tau \approx 200$ s.) These specifications are obtained with our calibration cell fitted in the sample cell holder of the microcalorimeter. Another type of calorimeter, using semiconductor detectors instead of thermocouples [18], was also used, giving approximately the same sensitivity and time constant under the same conditions. [This calorimeter was formerly commercialized by Arion, Corenc, France. The detectors, Peltier Kühlblöcke PKE 36 A 001, are available from Peltron GMBH, Nürnberg, F.R.G. (information due to the courtesy of P. Bazenet, Société Arion).] Its signal-to-noise ratio, about 10 times smaller than that of the Tian–Calvet, was not a problem in the usual range of the thermal effect in question (almost instantaneous delivery of $Q \geqslant 1$ J), with the advantage of being less expensive than a conventional Calvet microcalorimeter.

Cells

The cells (Fig. 1) are made of borosilicate glass. This material is resistant to corrosion, easily worked and allows visual inspection of the compounds under study. The Pyrex tube of nominal 17 mm OD, 1 mm thickness, is

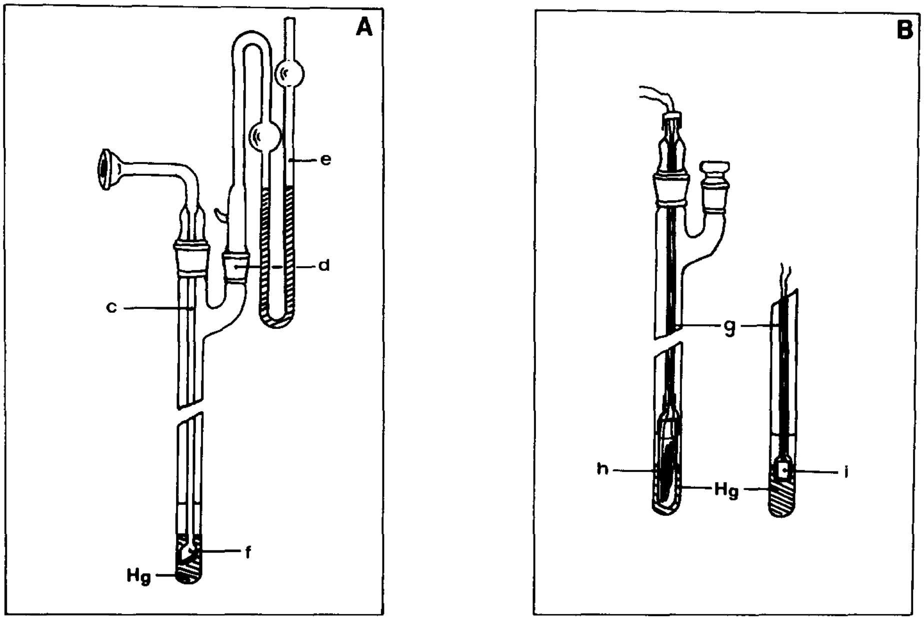

Fig. 1. A, The measuring cell; B, the Joule calibration cell. (c) Gas-injection tube; (d) liquid-introduction opening; (e) small U-tube mercury manometer; (f) sintered-glass valve; (g) supporting tube; (h) precision resistor; (i) Vishay thin-film resistor.

carefully chosen from a stock to fit the calorimeter cell-holders. Carefully checked test tubes were also used. The cell end, external to the calorimeter, is fitted with 2 female conical ground joints. On the measuring cell (Fig. 1A), one maintains the gas-injection tube (c), the other (d) holds a small U-tube mercury manometer (e) allowing the pressure inside the cell to be measured and providing insulation of the cell contents from atmospheric contamination. The gas-injection tube is maintained under vacuum, unless the gas is introduced in the cell. This system is made vacuum-tight by the use of a mercury valve like those used by Brown and Gintis [4]. The valve (f) constitutes the far end of the gas-injection tube fitted with a disk of sintered glass of appropriate porosity which is immersed into mercury. When the pressure in the gas-injection tube is slightly higher than that inside the cell, the gas is permitted to bubble through the mercury and comes into contact with the liquid to be studied placed over the mercury pool. When the gas is trapped or the gas-injection tube evacuated, the mercury is maintained against the sintered glass. The capillary forces prevent the mercury to flow through the porous glass if the porosity is suitably chosen (No. 4, diameter of pores, 10–20 10^{-6} m). If the porosity is too low, gas injection may be difficult.

The calibration cell was constructed to reproduce the measurement conditions as closely as possible. It is well known that the best accuracy in a calorimetric measurement is obtained when the calibration is performed on exactly the same experimental set-up as that used for measurement [19], including the location of the heat sources. In the present case, this is not possible because of the space limitation and corrosion problems, so we chose to build a calibration cell (Fig. 1B) having thermal characteristics very close to those of the measuring cell. We used the same external glass envelope as for the sample measurements. The tube (g) supporting the resistor is similar to the gas-injection tube in the measuring cell. The heat is generated near the mercury–liquid interface. In fact we have found that the height of liquid present in the cell does not affect the calibration constant if this height is maintained ≤ 60 mm from the far end of the cell. As the level of the liquid comes close to the upper end of the surface covered by the thermocouples (70 mm height) the calibration constant decreases due to heat loss at the upper part of the measuring volume [19].

Calibration system

Absolute calibration is realized by the Joule effect. A regulated power supply (EJP 30, Setaram, Lyon, France) delivers nominal currents between 0.1 and 17.32 mA in 12 steps, with an accuracy of 10^{-3} and a stability of 10^{-4}. The true current is checked by measuring the e.m.f. at the precision resistor (h) (1528.3 ± 0.1 Ω at 298 K, constantan) with a digital multimeter (172, Keithley, Cleveland, OH). The current was also checked by measuring the voltage drop at a high precision 100 Ω resistor inserted into the circuit. The value obtained this way agrees with the value measured across our heating resistor, and therefore only the last method of measurement is used in routine calibrations. An effective way to replace the tedious making and measuring of precision Joule resistors is to use a Vishay thin-film resistor (Sfernice, Nice, France). These resistors, with epoxy case, are small, light and have high specifications: precision = 5×10^{-5} (2×10^{-5} upon request); temperature coefficient = ± 1 ppm K^{-1} (0–60 °C); long-term stability (25 ppm: 1 year; 50 ppm: 3 years) and negligible inductance. We used a 1000 Ω (0.3 W; 0.8 g; $10 \times 9 \times 3.5$ mm; precision, 5×10^{-5}) fixed with epoxy resin to the glass tube shown on Fig. 1B(i). The time is measured with an electronic time counter (built in the laboratory) based on a 1 MHz quartz oscillator.

Vacuum line and calibrated volume

The measuring cell is connected to a vacuum line (Fig. 2), which permits the purification, transfer and measurement of the reactive gas. The original mercury diffusion pump, backed by a double-stage rotary pump, required efficient trapping to avoid backstream of mercury vapor. It was replaced by an integrated pumping system (j) including a roughing line and an oil

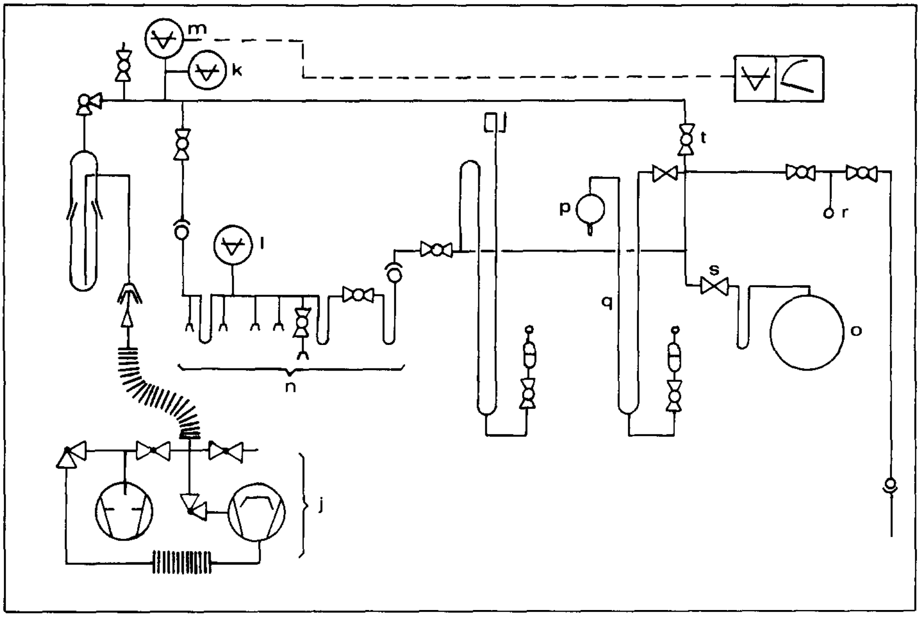

Fig. 2. Schematic of the vacuum line. (j) Integrated pumping system; (k) and (l) Bourdon gauges; (m) Penning gauge; (n) introduction-purification part; (o) 1-l flask; (p) calibrated measuring bulb; (q) U-tube manometer; (r) small injection bulb; (s) mercury valve(s); (t) greased stopcock(s).

diffusion pump (PD 40 L, Leybold-Heraeus, Köln, F.R.G.; pumping speed, 40 l s^{-1}; ultimate pressure, 10^{-6} mbar with Diffelen normal oil). The pumping system is connected to the borosilicate glass line by a glass-to-metal welding. Oil backstream or pump contamination is avoided by using an LN_2 trap between the line and the pumping unit. Rough pumping is controlled by Bourdon gauges (k, l), high vacuum by a cold cathode ionization (Penning) gauge (FA 101, Alcatel, Paris, France) (m). The vacuum ground joints, stoppers and valves are lubricated with Apiezon low vapor-pressure grease *. The first stage of the vacuum line is the introduction-purification part (n) that can be connected to gas cylinders or to synthesis apparatus. The gas introduced into the line is purified by low-temperature traps (pentane or methanol slushes) and/or freeze–pump–thaw cycles, then it is stored in a 1-l flask (o). A fraction may be transfered to the measuring bulb

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* The various kinds of Apiezon (L, M, N) used in our line show almost no reaction with gases. The most reactive one, BF_3, produced only a slow blackening after several weeks of intensive use. Tests have shown that successive gas expansions in the vacuum line where the gas is in contact with grease, and trapping back to the measuring bulb, do not change the quantity of gas. This is an indication that there is no detectable reaction and that solubility in grease, if any, is reversible. If these problems are likely to occur with more reactive species, greased glass valves may be exchanged for high-vacuum greasefree PTFE stopcocks.

(p) which is accurately calibrated ($V = 151.5$ ml) as described later. The pressure in the calibrated bulb is determined by measuring the height difference between the mercury menisci in the two arms of a wide-bore (10 mm) U-tube manometer (q), by means of a cathetometer with a resolution of 10^{-2} mm. (The use of mercury manometers and the associated problems: Hg purity, glass cleanliness, optical measurements, etc, have been recently reviewed [6].)

Constant-temperature room

The whole apparatus is located in a constant-temperature room of approximately 130 m^3. The temperature is regulated by a 3.3-kW heater appliance and two 2.4-kW air conditioners. The temperature probe is a mercury-contact thermometer triggering through a primary low-power relay, a high-power relay being connected to the heating/cooling devices. Depending on the season and weather, heating or cooling (or both) are applied. Even in the heating mode the air is always cycled by the air conditioners for temperature homogeneity. The temperature gradient within the room is less than 0.5 °C and temperature variations near the instruments are less than ±0.1 °C.

Data acquisition

The voltage output of the Tian–Calvet microcalorimeter, v_t, is sent to a high input-impedance graphic recorder (Servotrace PE, Enertec Schlumberger Sefram, France) and simultaneously to an amplifier (A 31, Setaram). The amplified signal is treated by an integrator for calorimetry and DTA (2105 M, Delsi, formerly LTT, France). This method proved to be very efficient in our case, where we have a stable baseline allowing many measurements the same day on a same sample solution. The area under the curve, $v_t = f(t)$, can be integrated by periods of chosen time interval (between 1 and 999 s). In the case of our experiments on acid–base reactions, the heat is produced very rapidly (a few seconds) and we observe a ballistic curve [15,16]. For our calorimeter, fitted with the gas–liquid cell, $t_{1/2} \approx 150$ s and we have chosen this time interval for integration sampling; the settling time is approximately equal to $10t_{1/2}$. The baseline is also sampled before and after the peak and if necessary corrections are applied for the baseline drift. We assume the drift to be linear as a function of time. The applied correction is always small ($\leqslant 1\%$ of the peak area), otherwise the measurement is discarded.

The theory of the Calvet microcalorimeter shows that the ballistic peak height H, measurable on the recorded graph, is proportional to the surface S under the curve [15]. Under given conditions the ratio S/H must be constant, and this property is used to check the consistency of a series of measurements or of one series with others under the same conditions, i.e. same cell, same quantities of mercury and solution (using dilute solutions the change in solute has very little effect on cell thermal parameters). Departure from this law, in general S/H too high or increasing along a series, as compared to a constant S/H with a normal series, is the indication of a slow secondary thermal effect associated with either chemical reactions (polymerization, isomerization, decomposition with formation of new solutes or new gases) or physical phenomena (crystallization, precipitation). This gives a distinct advantage over the "pseudo-adiabatic" calorimeters which simply integrate all sources of heat, without discriminating between their individual rates of heat generation.

CHECK OF THE CHEMICAL STATE OF THE REACTION PRODUCTS

Everyone recognizes the necessity to work with carefully purified compounds and under well-controlled conditions (initial state) but in general less accent is put on the need for the characterization (qualitative and quantitative) of the final state: the reaction products. Our method allows us to check the stoichiometry of the reaction (as described later). The nature of the reaction product(s) can be checked by spectroscopy, generally infrared or nuclear magnetic resonance, directly on the calorimetric solution, when the study is carried out in a suitable solvent.

DESCRIPTION OF A TYPICAL SERIES OF MEASUREMENTS [20]

The cell, containing 50 g of mercury, is put into the calorimeter and connected to the vacuum line. By the opening (d in Fig. 1A) a known amount of a compound is put in the cell, usually as a solute in 3 cm^3 of a 0.1–1 mol l^{-1} (generally 0.5 mol l^{-1}) solution or as a bulk liquid, over the mercury valve and the external Hg manometer (e in Fig. 1A) is set in place. The gas-injection tube (c in Fig. 1A) is evacuated by pumping, for at least 1 h until a stable pressure is obtained (2–5 10^{-4} mbar). (The background pressure in our vacuum line is mainly due to mercury vapor.) The thermal equilibrium is obtained in 1–2 h. Volatile solvents like dichloromethane necessitate longer times, and are allowed to stabilize overnight to be in equilibrium with their own vapor pressure, as read on the external manometer (e in Fig. 1A). After measuring the pressure, in the calibrated volume (p in Fig. 2) the reactive gas is transfered by LN_2 trapping in a small bulb (r in Fig. 2) then injected into the cell by its natural expansion. The remaining gas is trapped back to the small bulb, then to the calibrated bulb, allowed to equilibrate at room temperature, and the new pressure measured. The reaction is usually complete in about 10 injections (for a 0.5 mol l^{-1} solution), resulting in a discontinuous titration.

DATA REDUCTION

For a complete reaction, between each quantity (n_i mol) of gas injected and the solute or the bulk liquid reactant, giving Q_i J, the enthalpy of reaction is given by $\Delta H_i^0 = Q_i/n_i$ ($P = 1$ atm; in the case of a volatile solvent like CH_2Cl_2 $P > 1$ atm, but the correction is negligible).

ΔH_i^0 for each injection, their mean and the corresponding confidence limits, usually at the 95% level (CL 95) are calculated. A study of concentration effects on ΔH^0 has shown that ΔH^0 is independent of the concentration in the range 0.3–1 mol l^{-1} within measurement uncertainties [21]. When there are no chemical or physical secondary effects the precision is rather good (0.2–0.5% within a set, 0.5–1% between sets). It is difficult to assess the accuracy of our method but agreement with literature values (see also the following discussion) suggests 1–2%.

The method described above is equivalent to a discontinuous titration. Thus, information about the stoichiometry of the reaction or even the equilibrium constant may be obtained from the study of the curve Q (total heat produced) vs. n (total quantity of gas introduced). Three cases were observed.

When the formation constant K is high, the complex formation is quantitative until the stoichiometry is attained. Thus a more or less sharp break is observed on the titration curve depending on K and the concentration of the solution (Fig. 3A). In this case the slope of the first, linear, part of the titration curve is equal to the enthalpy of reaction, which may be obtained from a least-squares fit. This is an alternative statistical method for calculating ΔH^0. If the curved part is not too long, the quantity of added gas for a complete reaction n_c is easily determined. The curve after the point of abscissa n_c is almost horizontal, because further addition of the reactive gas causes virtually no heat effect. Usually only a weak endothermic effect is observed due to solvent evaporation caused by gas bubbling. The intercept between the two lines gives n_c. If after the completion of the reaction the

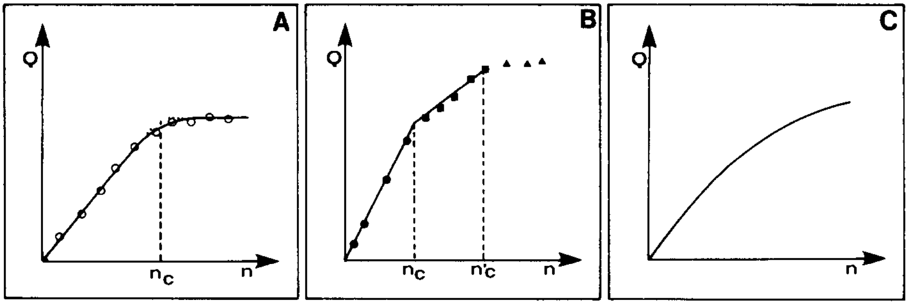

Fig. 3. $Q = f(n)$ curves: A, high formation constant; B, two-step reaction; C, low formation constant.

added gas is not soluble in the liquid contained in the cell, n_c may be calculated from the total amount of gas injected in the cell, corrected by the amount of unreacted gas. This last quantity is easily calculated from the cell volume and temperature, and the pressure due to the unreacted gas. Whenever applicable the two methods agree within a few percent.

We have also obtained titration curves (Fig. 3B) corresponding to a two-step reaction [22] giving two ΔH^0 and n_c values (in general $n'_c = 2n_c$).

When the formation constant is low, a continuous curve rather than straight-line parts is obtained (Fig. 3C). The general case has been reviewed in detail by several authors [23–26], but in the case of gas–liquid reactions a new problem arises: the unreacted gas may not be soluble enough in the reaction medium, so that only the first part of the curve is workable. Even with this limitation a method for the estimation of K and ΔH was devised [27,28].

CALIBRATION, ACCURACY AND PRECISION

Calorimetry

The absolute calibration of the system is obtained using the Joule effect with high accuracy. Electrical readings (resistance, current, voltage) are measured with a 10^{-4} uncertainty, as well as the time, giving an uncertainty of about 3×10^{-4}. The calibration constant obtained by the Joule effect can be obtained with a confidence interval of about 0.1% (at the 95% level). This calibration obtained with a cell set-up very similar to the true experimental conditions is believed to be not only precise but accurate. The constant is very stable as a function of time (range of variation: 0.5% over a period of 5 years).

Gas measurements

The uncertainty on the volume of the glass bulb, calibrated by weighting distilled and degassed water at a measured temperature with correction for air buoyancy, may be estimated as 3×10^{-4}. The pressure P inside the bulb is given by

$$P = \mu g h$$

where h is the mercury height at room temperature T, μ is the volumic mass of Hg at the same temperature (taken from ref. 29) and g is the acceleration due to gravity. The standard value of g [29,30] was used. The value calculated using Helmert's equation [29] differs only by 0.02% for the latitude and elevation of our laboratory. For instance one obtains

$$P(295.15\mathrm{K}) = 132.795h(\mathrm{Pa})$$

An equation of state has to be chosen to calculate the amount of gas. For the low pressures used in our case ($P < 4 \times 10^4$ Pa) we suppose a quasi-ideal behavior. Nevertheless, we checked this assumption in the case of BF_3, using Van der Waals' equation with the coefficients a and b calculated from the critical constants [31]. In the highest-pressure case, the amounts of BF_3 obtained from the ideal gas law and Van der Waals' equation differ only by 0.071% and the systematic error arising for non-ideality is usually less than 0.05%, so it is negligible when compared to the confidence interval of our measurements.

The purity of the reactive gas has to be taken into account. For instance BF_3 may contain 0.4% of $N_2 + O_2$ which can be easily removed by freeze–pump–thaw cycles. The availability of "electronic grade" gases is the best way to avoid the purification problem. The precision on the amount of gas injected depends on the uncertainties on 4 mercury-column-height readings, i.e. pressure before and after the injection and on the temperatures at which the heights are read. The mercury-column heights are read to the nearest 10^{-2} mm giving relative uncertainty of less than 10^{-3} on a typical difference of about 2 cm. It was shown that the main cause of error is the difference of temperature between the two pressure measurements [32] (before and after injection) giving a precision on P ranging from 0.5 to 1% under usual conditions.

Repeatability and reproducibility

The repeatability (same sample, same conditions, same analyst) of our measurements given as CL 95 is generally in the range of 0.5–1%. For a long-term repeatability (several years between the set of measurements, different samples, different analysts but same conditions) the precision did not vary.

We think that systematic errors on ΔH^0 are about 0.2%: 0.1% on the calibration constant, 0.03% on volume calibration and 0.05% for departure from the ideal gas law. Other contributions of this order of magnitude may arise from the small differences between the measuring and calibrating cells, and from batch-to-batch variations in the purity of the gas.

The reproducibility (between different laboratories) is more difficult to estimate due to the lack of recommended secondary standards for gas–liquid reactions. Nevertheless a possible one may be the reaction

$$BF_3(g) + \text{pyridine(soln)} \rightarrow \text{complex(soln)}$$

at 298.15 K in nitrobenzene.

The results obtained in our laboratories [20] agree within 0.5% with those obtained by Brown and Gintis [4] 30 years ago using a very different calorimetric procedure. A comparable reproducibility is also obtained when one substitutes tetrahydropyran [4] for pyridine.

Attempts to devise a more universal secondary standard, comparable to established thermodynamic measurements such as

$HCl(g) + H_2O(l)$

$HCl(g) + NaOH(aq.\ soln)$

or

$HCl(g) + TRIS(aq.\ soln)$

were not successful: the settling time was very long, giving uncertain integrations. (TRIS = tris(hydroxymethyl)aminomethane.)

Visual inspections showed inhomogeneous solutions (density gradient) and the long settling time was attributed to slow diffusion of ionic species in the aqueous solution. A mixing device must be used for these systems, but might introduce some additional errors.

APPLICATIONS

The method we have described has been applied in our laboratories to different gases and liquids but the most studied reaction was

$$BF_3(g) + B(soln) \rightarrow B{:}BF_3(soln) \qquad (2)$$

as a model of Lewis acid–base interactions. The most studied family of bases B was that of carbonyl compounds studied in dichloromethane solution.

Experimental values may be found in a series of papers entitled "Basicity of the carbonyl group" (Basicité du groupement carbonyle), BCG*. In a series entitled "Chimiometrie de la basicité" (Chemometrics of the basicity), CB, the second paper [44] also contains many experimental values for other various carbonyl compounds. 37 values for *ortho-*, *meta-* and *para-*substituted pyridines are reported in the first paper of the CB series [45].

Gas–liquid reactions involving phosphorus compounds gave insight into the substituent effects on the complexation of gaseous BF_3 with the PO or the PS group of heterocycles containing the phosphorus atom. These experiments were run in nitrobenzene solution [46–48]. The reactivity of gaseous BF_3 was also studied toward phosphorus compounds as bulk liquid [49] and the enthalpy of isomerization (slow reaction) of the trimethylthiophosphate and the trimethylselenophosphate were measured [50].

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* BCG: part 1 in the series, XC_6H_4CHO [33]; part 2, C_6H_5COX [34]; part 3, cyclohexenones [35]; part 4, CH_3COR [36]; part 5, cyclic ketones [37]; part 6, *p*-substituted *N*-ammoniobenzamidates [38]; part 7, cyclohexenones and acetophenones [39]; part 8, ethyl benzoates [28]; part 9, enamino-ketones [40]; part 10, β-substituted α,β-unsaturated ketones [41]; part 11, XC_6H_4CHO (revised and enlarged set of data) [42]; part 12, acetophenones and *N*,*N*-dimethylbenzamides [43]. Data for camphors are also available [32].

Diborane B_2H_6 was also used in studies of phosphorus and arsenic bases in benzene solution: PPh_3, $AsPh_3$ and $Ph_2PCH_2CH_2AsPh_2$ [22], (XYZ)P [51] and $(R_2N)_{3-n}(RO)_nP$ [52]. B_2H_6 was synthesized in a glass apparatus connected to our vacuum line.

In our last published report, our studies with BF_3 were enlarged to encompass the common organic functions, arriving at a donicity scale for nonprotogenic solvents for more than 75 compounds commonly used as solvents [20].

Another slow phenomenon, as compared to complexation, is polymerization. The corresponding enthalpy of polymerization, promoted by BF_3, was measured for olefinic compounds (alkenes as bulk liquid [53], stilbenes in dichloromethane solution [54]).

The removal of the acid gases (H_2S and CO_2) from natural and refinery gas is commonly accomplished by absorption in aqueous alkanolamine solutions and the solubilities of these gases in mono-, di- and triethanolamine have been thoroughly studied but the enthalpies of solution obtained from these data are still given without any information about precision [55]. Our earlier calorimetric measurements [56,57] (research supported by SNEA (P), France) are in good agreement with data obtained from solubilities.

It will be noted that more frequent cleanings of our vacuum line are in order when using H_2S, which reacts slowly with mercury.

We have also manipulated other gases than those mentioned above. The aim was to carefully control the solution of gaseous Lewis bases, such as $N(CH_3)_3$ and $O(CH_3)_2$, in CH_2Cl_2 for further basicity measurements [58] toward BF_3 according to reaction (2).

Gaseous HCl can be handled without any particular problems, but its mixing with aqueous solutions needs further study.

Measurements [59] of the enthalpy of solution of gaseous $S(CH_3)_2$ in water were done with a view to complete a thermodynamic cycle involving gas-phase and aqueous-phase basicities like those used by Jones and Arnett [60] or Taft et al. [61,62].

CONCLUSION

In the present paper we reported our efforts to realize a convenient, easy-to-use apparatus for microcalorimetric measurements of enthalpies of solution of gases in liquids. It was shown that the method provides the user with an efficient tool for the study of different reactions, either fast, such as complexation, or slow, such as isomerization and polymerization, with precision and accuracy.

In the case of studies of interactions between a gas and a reactive solute dissolved in an inert solvent, we take advantage of the fact that our method works as a discontinuous titration, and allows careful control of the evolution of the reaction as well as of the final state of the product(s).

In closing, the main applications of this method in our laboratories have been presented. The hundreds of complexation enthalpies obtained in this way have led to new insight in the physical organic chemistry field of substituent and solvent effects. Other exploratory studies have shown that this technique can be applied to other fields, such as polymer chemistry or natural gas refining.

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