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RECENT PROGRESS IN TITRATION CALORIMETRY

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Research developments in titration calorimetry over the past ten years by personnel at the Thermochemical Institute have resulted in new techniques and instrumentation that have greatly increased the usefulness of calorimetry in the study of chemical problems. During this time, problems associated with the components of the calorimeter (i.e., constant temperature bath, constant rate buret, reaction vessel, temperature sensing circuit, and data analysis procedure) have been solved so that the continuous titration method now gives results comparable in accuracy to those obtained with conventional solution calorimeters. These developments have opened new avenues of research in the fields of biochemistry, microbiology, and environmental analysis.

Equipment and data analysis

We have developed isoperibol [1, 2] and isothermal [3] reaction vessels which operate with 2 ml of solution in the reaction vessel and burets capable of delivering titrant at rates $<10\ \mu l/min$ with a variation in the delivery rate of $<0.1\%$. The development of micro titration calorimeters means that less material is needed for the same accuracy of determination, or that more concentrated solutions may be studied with the same amount of material with consequently larger temperature changes and hence increased accuracy. Details of reaction vessels designed for small volume isoperibol and isothermal titration calorimeters are shown in Figures 1 and 2. Although the design of the small vessels is simply a matter of scaling down the large vessel to the required size, other difficulties are encountered. One difficulty in the isoperibol instrument is that the modules of heat loss increases exponentially as the vessel size decreases. In addition for both isoperibol and isothermal calorimeters the relative importance of heat inputs from stirring and solvent evaporation increases as the volume of the dewar decreases. Accurate data analysis involves determination of these effects as a function of volume of solution in the reaction vessel. The development of small volume isothermal reaction vessels has led to a design where the reaction vessel temperature sensing and control is completely separate from the reaction vessel. This has resulted in the design of isothermal flow or batch instruments [4]. The accuracy and precision of the instruments have been checked by measurement of the heat of ionization of water (1 – 3,5) determined by conventional solution calorimetry as 55.79 ± 0.06 kJ/mole [6]. Results are summarized in Table 1.

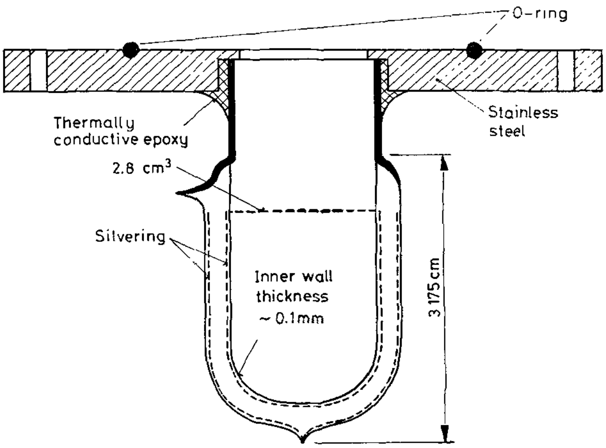

Fig. 1. Isoperibol reaction vessel

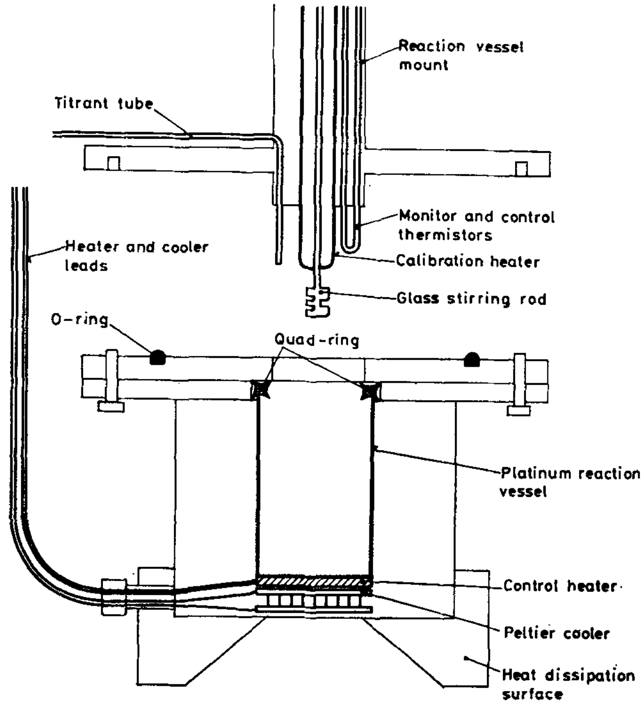

Fig. 2. Isothermal reaction vessel

Table 1

Heat of ionization of H_2O at 25° corrected to $\mu = 0$

Calorimeter	$\Delta H°$ (kJ/mol)	Ionic strength range
50 ml isothermal	55.77 ± 0.02	0.01 — 0.0005
3 ml isothermal	$55\ 83 \pm 0.14$	0.01 — 0.001
3 ml isoperibol	55.88 ± 0.28	0.01 — 0.003

Thermodynamic applications

We have previously shown that calorimetric data may be used to obtain both ΔG and ΔH values for reactions in solution [7–10]. The large amount of data obtained by a titration instrument make possible the study of complex systems. The general utility of a calorimeter as an instrument for detecting reactions makes possible the study of a wide range of systems. Thus, for example, adsorption capacities, equilibrium constant and enthalpy change values for the interaction of aromatic compounds with molecular sieves [11] or the study of metal ion complexation with macrocyclic polyether ligands in a wide variety of solvents [12–14] may be readily determined by this technique. Titration calorimetry is particularly useful for the determination of reaction stoichiometry. This is illustrated by the results in Fig. 3. Titration of Ag^+ with 1,10-dithia-18-crown-6 (b) gives an indication of only 1 : 1 complex formation. In contrast, titration into the analog 1,4-dithia-18-crown-6 (a) indicates both 1 : 1 and 2 : 1 crown : Ag^+ complexes are formed. Log K, ΔH, and ΔS values may all be calculated from the calorimetric data for these reactions.

Biological and biochemical applications

The application of titration calorimetry to the study of complex systems is well illustrated by studies on biological systems. Calorimetry has been used to study the details of adsorption of surfactants by proteins [15] and membranes [16], of proteins by membranes [17], and the interaction of metal ions or protons with proteins [18]. Calorimetry, and particularly isothermal calorimetry, can often be used to study long-term reactions such as biological growth processes. Extensive applications of this type have been published by Wadsö and co-workers at Lund. Work in our laboratory has included the study of the influence of cytotoxic agents on thermogenesis in bacteria [19] and the red blood cell [20], and the study of cell transformation [21].

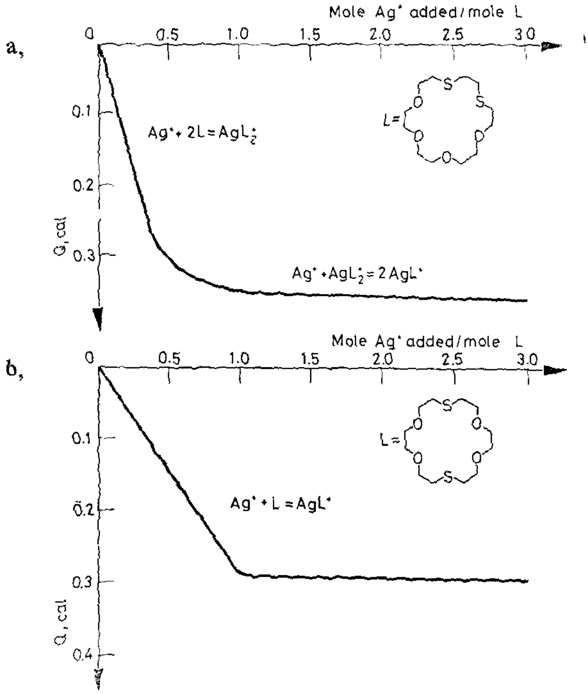

Fig. 3. Calorimetric titration curves for the titration of 1.4-dithia-18-crown-6 (a) and 1.10-dithia-18-crown-6- (b) with Ag^+

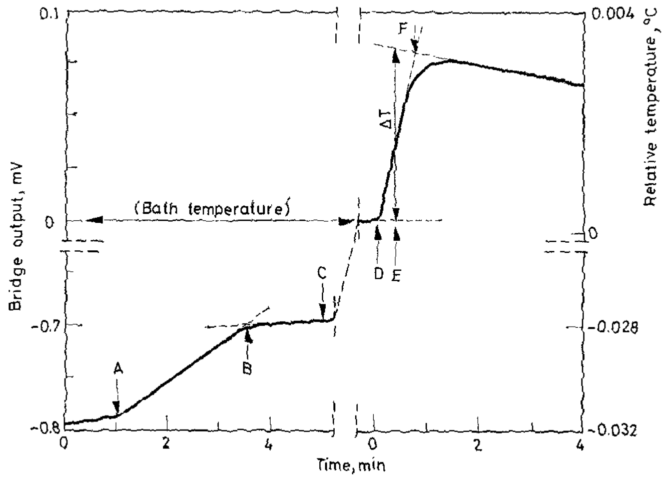

Fig. 4. Typical curves for thermometric titration of S(IV) with $K_2Cr_2O_7$ and DIE determination of sulfate with $BaCl_2$. The buret is turned on at *A* and off at *C*. At *D* the $BaCl_2$ is injected

Environmental chemistry

Personnel at the Thermochemical Institute are now involved in the use of calorimetry as an analytical tool to study particulate sulfur chemistry. It has been shown that titration calorimetry is ideally suited for the identification of many components of aerosols since it has wide range applicability to the detection of many species, is generally free of interferences that effect conventional spectrophotometric or potentiometric methods, and has sufficient sensitivity for use in environmental programs. Redox titration with an oxidizing agent has been shown to be useful for determining Fe(II), S(IV), As(III) and other reducing agents in particulate samples [22, 23]. Direct injection enthalpimetry has been used to determine levels of sulfate [22] and nitrite [24]. The titration of sulfite with dichromate, followed by the DIE determination of sulfate is illustrated in Fig. 4. Acid-base titrations in either aqueous [25] or nonaqueous [26] solvents have been used to probe in detail the identity and amounts of both strong and weak acids in collected aerosols. In Fig. 5 is shown data obtained by titration of an aqueous extract of a New York City aerosol with NaOH and $HClO_4$ using a micro titration calorimeter equipped with a pH probe. Since the problem of identification of specific compounds present in environmental atmospheric pollution is essential to the establishment of meaningful and effective control programs, calorimetry should make a significant contribution to this field of science.

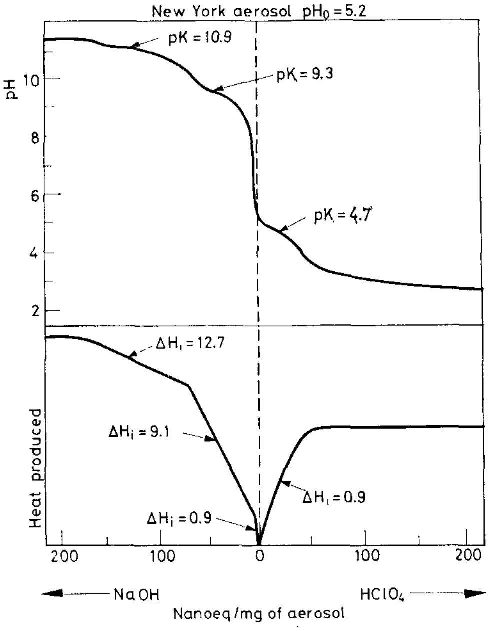

Fig. 5. Combined pH and calorimetric titration of an urban aerosol extract

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RÉSUMÉ — Les recherches effectuées durant les dix dernières années par le personnel de l'Institut de Thermochimie ont eu pour résultat la mise au point d'appareils nouveaux qui augmentent, considérablement l'applicabilité de la calorimétrie à l'étude des problèmes chimiques. Ainsi les problèmes associés aux composants d'un calorimètre (c'est-à-dire bain à température constante, burette à vitesse constante, récipient réactionnel, circuit détecteur de température et procédés d'analyse des données) ont été résolus. C'est pourquoi la technique du titrage en continu donne maintenant des résultats d'une exactitude comparable à celle obtenue avec les calorimètres en solutions conventionnels. Ces développements ont ouvert de nouvelles perspectives de recherche dans les domaines de la biochimie, de la microbiologie et des analyses liées à la protection de l'environnement.

ZUSAMMENFASSUNG — Die Fortschritte der Forschung auf dem Gebiete der Titrationskalorimetrie, welche in den vergangenen Jahren von Mitarbeitern des Thermochemischen Instituts erreicht worden sind, führten zu neuen Techniken und neuer Instrumentation, die die Einsatzfähigkeit der Kalorimetrie zur Untersuchung chemischer Probleme wesentlich erhöhten. Während dieser Zeit wurden Probleme in Zusammenhang mit den Bestandteilen des Kalorimeters (d.h. Konstanttemperaturbad, Bürette mit konstanter Geschwindigkeit, Reaktionsbehälter, Temperatur, Wärmefühler-Stromkreis und Datenverarbeitungsvorgang) gelöst, so daß die kontinuierliche Titrationsmethode jetzt Ergebnisse von einer Genauigkeit liefert, welche mit der in herkömmlichen Lösungskalorimetern erhaltenen vergleichbar ist. Diese Entwicklungsarbeit eröffnet neue Wege der Forschung auf den Gebieten der Biochemie, Mikrobiologie und Umweltschutzanalyse

Резюме — Исследования в области калориметрического титрования, проведенные сотрудниками Термохимического института за прошедшее десятилетие, привели к методам и технике, что значительно увеличило возможности использования калориметрии при изучении химических проблем. В течении этого времени были решены проблемы, связанные с компонентами калориметра: баня с постоянной температурой, бюретка с постоянной скоростью, реакционный сосуд, температурно-чувствительная цепь и метод анализа данных. Благодаря этому, метод непрерывного титрования теперь дает результаты, сравнимые по точности с теми, что были получены обычными калориметрами. Это развитие открыло новые пути исследования в области биохимии, микробиологии и окружающей среды.