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# APPLICATIONS OF SOLUTION CALORIMETRY TO A WIDE RANGE OF CHEMICAL AND PHYSICAL PROBLEMS *

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## ABSTRACT

Brief descriptions are given of several calorimetric techniques and the application of these techniques to the study of a variety of chemical problems is tabulated. The techniques described are titration, direct injection, flow and batch calorimetry. Applications of calorimetry in biochemistry and biology and in inorganic and organic chemistry are presented in two tables. The material presented demonstrates the potential of calorimetry in research, industry, analytical chemistry and clinical analysis.

## INTRODUCTION

The amount of success experienced by an investigator in science or engineering depends to a large extent on his or her ability to use in a creative manner available experimental techniques to study a problem. In choosing a method for use in solving a problem or studying a reaction, several questions should be considered.

(1) What are the properties of the materials involved in the system?

(2) What types of data are needed to solve the problem?

(3) How can the properties of the system under study be coupled with available experimental techniques to obtain the desired data?

(4) Which technique is the most time and cost efficient?

One property that is present in nearly all chemical and physical processes is enthalpy change. The heat effects as processes proceed can be used to study a wide spectrum of chemical and physical phenomena. Thus, calorimetry is useful in that it uses heat production (or absorption) as a probe to study and analyze processes.

Several techniques are used in calorimetry. The primary purpose of this paper is to present short descriptions of these techniques and show the types

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of problems which have been studied using them. The individual worker must decide whether or not a particular calorimetric procedure is the most time and cost-efficient method for acquisition of specific data.

Calorimetric techniques can be classified according to two criteria: (1) the method used to manipulate liquid solutions used in the calorimeter, and (2) the technique used to measure enthalpy changes and heat production rates (power) as a reaction proceeds in the calorimetric vessel. There are four general techniques used to manipulate solutions in a calorimeter: (1) titration, (2) direct injection, (3) flow and (4) batch.

Titration calorimetry consists of introducing a titrant into the reaction vessel at a known constant rate (continuous titration) or in small equal-volume amounts (incremental titration). Motorized syringe-type precision burets are used generally, but gravity-flow thermostatted burets have been used also. The temperature or heat production in the reaction vessel is monitored either as a function of titrant added or as a function of time if the titration is performed in the continuous mode. This technique is sometimes referred to as thermometric enthalpy titration or TET [1].

Direct injection calorimetry consists of injecting quickly an excess of titrant into the reaction vessel and measuring the heat flux or the temperature change caused by the added titrant. This technique is sometimes called direct injection enthalpimetry or DIE [2].

Flow calorimetry is characterized by a reaction vessel configuration where either two or more streams of reactants are pumped into a mixing chamber or tube where they mix and react. From there they flow on through and out of the calorimeter into a waste vessel. The heat produced by the reaction is recorded as a temperature change in the reaction stream or as heat flux from the reaction vessel to a surrounding heat sink or peltier cooler. There are many possible variations in flow configuration such as mixing cells, flow-through cells, stopped-flow devices, steady-state devices, etc. The interested reader can find more detailed discussions on flow configurations in refs. 2 and 3.

Batch calorimetry refers to any calorimetric determination where no external mass is introduced across the vessel boundaries during the course of the determination. One batch configuration consists of a thin-walled glass capsule containing one of the reactants immersed in the other reactant solution. The reaction is initiated by breaking the capsule. In another common batch configuration, the vessel is constructed such that the reactant solutions are physically separated by a barrier but rotation of the vessel allows them to mix and react.

As mentioned previously, the second criterion for classification of calorimeters is the technique used to measure enthalpy changes and rates of heat production (power). There are five basic methods for determining these parameters: (1) isoperibol, (2) isothermal, (3) heat conduction, (4) adiabatic and (5) temperature scanning.

Isoperibol calorimetry is characterized by a dewar-type reaction vessel and constant temperature surroundings usually consisting of a thermostatted water bath. The reaction vessel is designed to be as adiabatic as possible thus inhibiting heat flux to the surroundings. Heat production is determined by measuring the temperature change and correlating it to the heat capacity of the vessel and its contents. Corrections must be made for non-reaction heating effects and heat leaks.

Isothermal calorimetry is characterized by the incorporation of a peltier cooler and variable-rate heater in the reaction vessel configuration. The peltier cooler cools the vessel at a constant rate and the heater is pulsed as needed to maintain the vessel and its contents at a constant temperature. When an exothermic reaction occurs, heat is produced and a lower heater pulse rate is required to balance the cooling effect of the peltier device. Conversely, for an endothermic reaction, a higher pulse rate is required to balance the energy effects of the reactions and the peltier cooler. The amount of heat produced by a reaction is determined by observing the time that the heater has to remain on to balance the peltier cooler and comparing this time to heater requirements during base-line conditions.

Heat conduction calorimetry, developed by Calvet and discussed in ref. 3, is characterized by a vessel that is in thermal contact with a surrounding heat sink. This thermal contact is achieved by placing either thermocouples or thermoelectric devices between the vessel and the heat sink. The thermocouples are connected in series as are the junctions in the thermoelectric devices. As a reaction releases heat, a slight temperature gradient develops between the reaction vessel and the heat sink. This causes a small voltage to be produced by each thermocouple or thermoelectric junction which, because of the series connection, results in a much larger overall voltage. The voltage produced can be correlated to a specific rate of heat production (power) caused by the reaction taking place and from this rate enthalpy changes can be monitored and determined. Heat conduction calorimeters are sometimes referred to as "isothermal" heat conduction calorimeters, but this name is a misnomer. It is true that the temperature changes in the reaction vessel are kept to a minimum by heat conduction through the thermopile and hence, "quasi-isothermal" may be an appropriate term. However, if these calorimeters did operate in an isothermal mode, there could not be any temperature gradient between the vessel and the heat sink because no change in temperature within the reaction vessel would be possible. If there were no temperature gradient, there could be no heat conduction and no voltage could be produced by the thermopile; hence, heat production could not be measured.

Adiabatic calorimetry, in theory, is very similar to isoperibol calorimetry. However, there is one main difference. Adiabatic calorimeters employ a heated shield that surrounds the reaction vessel. The temperature of the heated shield is maintained at the same temperature as the contents inside the reaction vessel. Thus, any significant temperature gradient between the

TABLE 1

Applications of calorimetry in biochemistry and biology

| Determination | Method [a] | Basic references |
|---|---|---|
| *A. Analytical determinations* | | |
| Antibiotics and drugs | Isoperibol cont. titr. | 7 |
| | Isothermal titration | 8 |
| | Isoperibol dir. inject. | 9, 10 |
| | Heat cond. flow | 8, 11, 12 |
| | Heat cond. batch | 8 |
| Bacterial count | Heat cond. flow | 3, 12, 13 |
| | Flow | 14–17 |
| | Heat cond. batch | 3 |
| | Batch | 13, 14 |
| Bacteriuria | Heat cond. flow | 12, 14 |
| | Flow | 15, 16–18 |
| | Not specified | 19 |
| Differences between sickle-cell and normal erythrocytes | Not specified | 19 |
| Endpoints (catalytic thermometric titrimetry) | Titration | 8 |
| Endpoints for coupled reactions with small $\Delta H$ values (chemical amplification) | Isoperibol | 20 |
| | Flow | 19 |
| | Not specified | 20–23 |
| Enzyme activity (enzyme assay) | Isoperibol cont. titr. | 7 |
| | Isothermal dir. inject. | 21 |
| | Isoperibol dir. inject. | 7, 15, 21 |
| | Heat cond. flow | 3, 15 |
| | Flow | 15, 17, 19–21, 24, 2 |
| | Heat cond. batch | 15, 20, 21 |
| | Batch | 3, 17, 25 |
| | Not specified | 17, 20, 21, 23, 25 |
| Enzyme inhibitor concentration | Direct injection | 3, 20, 21 |
| | Flow | 19–21 |
| | Not specified | 19–21 |
| Enzyme-linked immunosorbent assay | Semi-adiabatic flow | 20 |
| Heat production by mixed microbial cultures | Flow | 15 |
| | Not specified | 15, 16, 26 |
| Heat production by muscle and muscle protein reactions | Titration | 27 |
| | Heat cond. batch | 27, 28 |
| | Batch | 27, 28 |
| | Not specified | 27–29 |
| Heat production by organs, organ tissues and organites | Direct injection | 30 |
| | Isoperibol batch | 31 |
| | Heat cond. batch | 28, 31, 32 |

TABLE 1 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| Heat production by tissue cells in vitro | Heat cond. incr. titr. | 33 |
| | Heat cond. flow | 29 |
| | Isothermal batch | 18 |
| | Heat cond. batch | 29, 32 |
| Hormone activity (insulin) | Heat cond. dir. inject. | 3 |
| | Not specified | 25 |
| Immobilized enzymes for use in calorimetry | | 34–36 |
| Inorganic ions and small organic species found in body fluids | Isoperibol titration | 37 |
| | Direct injection | 37 |
| | Semi-adiabatic flow | 20 |
| | Flow | 37 |
| | Not specified | 19, 20, 37, 38 |
| Microbial contamination in water (e.g. sewage water, processed food, etc.) | Heat cond. flow | 13 |
| | Flow | 16 |
| | Not specified | 19 |
| Peroxides | Semi-adiabatic flow | 39 |
| | Flow | 25 |
| Protein | Isoperibol cont. titr. | 7, 18–20, 25 |
| Quantity of erythrocyte–protein binding sites on normal and sickeled erythrocytes | Isoperibol cont. titr. | 18, 24 |
| Stoichiometry for antigen–antibody interactions | Isoperibol cont. titr. | 7, 40 |
| Stoichiometry of metal ion binding to proteins, lipids and large biochemical molecules | Isoperibol cont. titr. | 18 |
| | Continuous titration | 40 |
| Substrates in binary mixtures with a single titration | Not specified | 20 |
| Substrates using immobilized enzymes | Isothermal cont. titr. | 18 |
| | Heat cond. flow | 3, 17, 18, 35, 41 |
| | Semi-adiabatic flow | 2, 15, 17, 18, 20, 25, 34–36, 39, 41 |
| | Thermistor enzyme probe | 9, 15, 18, 20, 25, 34, 42 |
| | Batch | 25 |
| Substrates using soluble enzymes | Isoperibol dir. inject. | 7, 9, 10, 15, 17, 19–21 |
| | Semi-adiabatic flow | 2, 34 |
| | Flow | 3, 15, 17, 19, 25 |
| | Heat cond. batch | 3, 15, 19 |
| | Batch | 3, 17, 19, 25 |
| | Not specified | 19–21, 23, 43 |

TABLE 1 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| Thermogram fingerprints for the identification of bacteria and yeasts | Heat cond. flow | 12 |
| | Flow | 15, 17, 44, 45 |
| | Heat cond. batch | 3, 26 |
| | Batch | 3, 14, 15, 17, 19, 44, |
| | Not specified | 16, 25, 26 |
| B. *Qualitative determinations of effects* | | |
| Antibiotics and cytotoxins (disinfectants) on heat production by bacteria (antibiotic–disinfectant sensitivity testing) | Isothermal titration | 18, 46 |
| | Heat cond. flow | 3, 8, 12, 46–52 |
| | Flow | 8, 15, 17, 18, 44 |
| | Isoperibol batch | 46 |
| | Heat cond. batch | 8, 46 |
| | Batch | 15, 44 |
| Antibiotics and cytotoxins on heat production by yeast cultures | Heat cond. flow | 8, 15, 46, 47 |
| | Flow | 48 |
| | Not specified | 48 |
| Blood coagulation on thermograms and correlation of peaks in thermograms to chemical events taking place | Heat cond. flow | 3 |
| | Adiabatic batch | 25 |
| | Batch | 3, 25, 53, 54 |
| Carcinogens on heat production by tissue cells | Isothermal batch | 18 |
| | Not specified | 28 |
| Competitive binding in biochemical molecule complexes | Continuous titration | 55 |
| Enzymes, hormones and other chemicals on tissue cell heat production (metabolism) | Titration | 27 |
| | Direct injection | 30 |
| | Heat cond. flow | 29 |
| | Heat cond. batch | 27–29 |
| Fertilizers, pollutants, and residual herbicides on biological activities in soils | Heat cond. batch | 3, 53, 56 |
| | Batch | 15 |
| | Not specified | 16 |
| Light on heat production by photoluminescent bacteria | Isothermal batch | 18, 24 |
| | Heat cond. batch | 43 |
| Metabolic blocking agents on cellulose heat production | Heat cond. batch | 8 |
| Insecticides and pheromones on power output of live insects | Heat cond. batch | 57 |
| Protein synthesis in a cell-free system on the thermogram | Heat cond. batch | 3 |
| Proton ionization by proteins, and correlation of the thermogram to functional groups in protein molecules | Isoperibol cont. titr. | 39, 40 |
| | Flow | 3, 40, 43 |
| Temperature, pH and normal and pathological conditions on heat | Heat cond. flow | 3, 29, 54 |
| | Flow | 15, 17, 25 |

TABLE 1 (continued)

| Determination | Method[a] | Basic references |
|---|---|---|
| production by erythrocytes, leukocytes and thrombocytes | Isothermal batch | 18 |
| | Heat cond. batch | 3, 15, 29 |
| | Batch | 3, 25, 53, 54 |
| | Not specified | 17, 19, 25, 54 |
| Type and quantity of energy supply, temperature, oxygen content of medium, pH, etc. on heat production by bacteria | Heat cond. flow | 3, 8, 12, 26 |
| | Flow | 15, 44, 46 |
| | Isothermal batch | 18 |
| | Heat cond. batch | 26 |
| | Adiabatic batch | 26 |
| | Batch | 15, 44, 46 |
| | Not specified | 19 |
| Type and quantity of energy supply, temperature, oxygen content of medium, pH, etc. on heat production by yeast cultures | Heat cond. flow | 3, 8, 48, 58 |
| | Flow | 48 |
| | Heat cond. batch | 3, 48, 58 |
| | Batch | 48 |
| | Not specified | 26, 45 |
| C. *Enthalpy change, $\Delta$H, determinations* | | |
| Antibody–antigen interactions | Continuous titration | 18, 39 |
| A slow process | Flow | 22, 59 |
| | Not specified | 3 |
| Biochemical processes, also $\Delta C_p$ values | Not specified | 19, 22 |
| Biochemical redox reactions not involving a catalyst or enzyme | Not specified | 19 |
| Conformational changes in macromolecules (proteins) | Batch | 24 |
| Coupled reactions for study of a reaction with a low $\Delta H$ (amplification of reaction enthalpies) | Not specified | 20–22 |
| Enzyme-catalyzed reactions | Heat cond. batch | 19, 60 |
| | Isoperibol | 61 |
| | Not specified | 19, 24, 43, 61, 62 |
| Enzyme–inhibitor or substrate–inhibitor binding | Titration | 40 |
| | Isoperibol batch | 3 |
| | Flow | 40 |
| | Not specified | 40 |
| Gas absorption by hemoglobin ($O_2$, $CO_2$, CO) | Flow | 24 |
| | Batch (modified) | 24, 43 |
| | Not specified | 22 |
| Hapten–antibody binding | Continuous titration | 39 |
| | Heat cond. flow | 3 |
| | Not specified | 24,43 |
| Isomerization of sugars | Not specified | 62 |

TABLE 1 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| Macromolecule–ligand interactions | Batch | 19 |
| | Not specified | 19, 22, 43 |
| Metal ion-antibiotic complexes (see also metal–ligand headings in the organic–inorganic table) | Batch | 8 |
| Metal ion–protein interactions | Isoperibol cont. titr. | 18 |
| | Not specified | 19 |
| Protein–erythrocyte binding (normal and sickle cell) | Isoperibol Cont. Titr. | 18, 24 |
| Proton ionization from proteins | Isoperibol cont. titr. | 40 |
| | Titration | 19, 24 |
| | Flow | 3, 19, 40, 43 |
| | Not specified | 24 |
| Protein–protein binding | Heat cond. cont. titr. | 27 |
| | Flow | 43 |
| | Batch | 3 |
| | Not specified | 19, 24, 43 |
| Protein–surfactant binding | Batch | 3 |
| D. *Equilibrium constant,* K, *determinations* | | |
| Antigen–antibody interactions | Continuous titration | 18, 39 |
| Biological macromolecule–ligand interactions | Batch | 19 |
| | Not specified | 19, 22, 43 |
| Erythrocyte–protein interactions for normal and sickled erythrocytes | Isoperibol cont. titr. | 18, 24 |
| Hapten–antibody interactions | Continuous titration | 39 |
| Protein–protein interactions | Heat cond. cont. titr. | 27 |
| | Not specified | 19 |
| Proton ionization from proteins | Isoperibol cont. titr. | 40 |
| | Titration | 19, 24 |
| | Flow | 19 |
| | Not specified | 19, 24 |
| Substrate–inhibitor and enzyme–inhibitor interactions | Isoperibol batch | 3 |
| | Not specified | 21, 22, 40 |
| E. *Kinetic parameter determinations* | | |
| Antibiotic and drug action on microbial cultures | Heat cond. flow | 8, 24, 46 |
| | Flow | 17 |
| | Batch | 17 |
| | Not specified | 16 |
| Enzyme–substrate and enzyme–inhibitor reactions (i.e. $V_{max}$, $K_m$, etc.) | Isoperibol dir. inject. | 20 |
| | Direct injection | 20, 21, 39, 63 |
| | Heat cond. flow | 3, 64, 65 |
| | Flow | 19–21, 24, 43, 64 |

TABLE 1 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| | Heat cond. batch | 3, 19 |
| | Batch | 19 |
| | Not specified | 20–22, 24 |
| Non-enzyme biochemical-type reactions | Isoperibol dir. inject. | 24 |
| | Heat cond. flow | 59 |
| | Flow | 22, 65 |
| | Not specified | 3 |

[a] Isoperibol cont. titr. = Isoperibol continuous titration; Isoperibol dir. inject. = Isoperibol direct injection; Heat cond. flow = Heat conduction flow; Heat cond. batch = Heat conduction batch; Isothermal dir. inject. = Isothermal direct injection; Heat cond. dir. inject. = Heat conduction direct injection; Isothermal cont. titr. = Isothermal continuous titration; Heat cond. incr. titr. = Heat conduction incremental titration; Heat cond. cont. titr. = Heat conduction continuous titration.

reaction vessel and its surroundings is eliminated and for all practical purposes, heat leakage from the reaction vessel does not occur. Heat produced by the reaction is calculated from temperature change and heat capacity data.

Temperature scanning calorimetry is used to determine physical properties and constants such as specific heat capacities, entropies of fusion, and other phase changes which occur with changes in temperature and/or pressure. Temperature scanning calorimetry is beyond the scope of this paper. However, there are several review articles on the subject [4,5,6].

The information in Table 1 on applications in biochemistry and biology and in Table 2 on applications in inorganic and organic chemistry is intended to help the reader understand the potential that calorimeters possess as tools in research, industry, analytical chemistry and clinical analysis. Table 1 lists applications in biochemistry and biology in the areas of analytical and qualitative chemistry, and the determination of enthalpy changes ($\Delta H$), equilibrium constants ($K$) and kinetic parameters. Table 2 lists applications in inorganic and organic chemistry in the areas of analytical chemistry and the determination of enthalpy changes, equilibrium constants and kinetic parameters. Both tables list specific determinations which have been made, types of calorimeters which have been used and references to review articles, chapters in books, and, especially for recent literature, several primary sources. In those cases where the calorimetric technique used to measure enthalpy changes and heat production rates is not stated in the reference cited, the words "Not specified" are listed in the Method column. Additional information on the technique used is available in the original paper.

TABLE 2

Applications of calorimetry in inorganic and organic chemistry

| Determination | Method [a] | Basic references |
|---|---|---|
| A. *Analytical determinations* | | |
| Active site distribution on a catalyst surface | Heat conduction | 66 |
| | Not specified | 67 |
| Active site inhibitors for catalysts | Not specified | 67 |
| Alcohols and phenols | Continuous titration | 68 |
| | Isoperibol | 9, 68 |
| | Flow | 68 |
| Aldehydes and ketones | Continuous titration | 68 |
| Amines, amides and anilides by calorimetric methods other than acid–base titration | Continuous titration | 68 |
| Anhydrides | Continuous titration | 68 |
| | Isoperibol dir. inject. | 68 |
| Carboxylic acids by calorimetric methods other than acid–base titration | Continuous titration | 68 |
| Cation exchange capacity for clays | Isoperibol cont. titr. | 69 |
| Chemical species in airborne particulate matter (air pollution) | Isoperibol cont. titr. | 70, 71 |
| Components in binary and ternary mixtures with a single titration | Continuous titration | 72, 73 |
| | Direct injection | 73 |
| | Flow | 74 |
| | Not specified | 73, 75 |
| Detergents | Continuous titration | 74 |
| Elements in their more common oxidation states | | |
| Li, Na, K | Continuous titration | 38, 74 |
| | Direct injection | 7, 38 |
| Be, Mg, Ca, Sr, Ba | Continuous titration | 7, 38, 74 |
| | Direct injection | 38 |
| | Semi-adiabatic flow | 39, 74 |
| | Flow | 38 |
| | Not specified | 76 |
| B, Al, Ga, In, Tl | Continuous titration | 7, 38, 74 |
| | Direct injection | 38 |
| | Semi-adiabatic flow | 74 |
| | Not specified | 76 |
| C ($CO_2$, $CO_3^{2-}$, $CS_2$, $CN^-$, $SCN^-$), Si ($H_2SiF_6$, $SiO_2$), Pb | Continuous titration | 38, 74 |
| | Direct injection | 38 |
| | Semi-adiabatic flow | 74 |

TABLE 2 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| | Flow | 38 |
| | Not specified | 76 |
| N($NH_3$, $N_2O_4$, $NO_2^-$, $NO_3^-$), P($PO_4^{3-}$), As, Sb | Continuous titration | 38, 74 |
| | Incremental titration | 38 |
| | Direct injection | 38 |
| O($H_2O$, $H_2O_2$, $O_2$), S(S, $H_2S$, $SO_2$, $S_2O_3^{2-}$, $SO_3^{2-}$, $SO_4^{2-}$, $S_2O_8^{2-}$), Se | Continuous titration | 38, 71, 74 |
| | Direct injection | 38 |
| | Semi-adiabatic flow | 7, 74 |
| | Batch | 38 |
| | Not specified | 74 |
| F, Cl, Br, I | Continuous titration | 38, 74 |
| | Direct injection | 38 |
| | Heat conduction flow | 38 |
| | Flow | 38 |
| Cu, Zn, Ag, Cd, Hg | Continuous titration | 33, 74 |
| | Direct injection | 38 |
| | Semi-adiabatic flow | 74 |
| | Not specified | 76 |
| Ti, Zr, V | Continuous titration | 38 |
| | Direct injection | 7, 38 |
| Cr, Mo, W | Continuous titration | 38, 74 |
| | Direct injection | 38 |
| | Not specified | 76 |
| Mn, Fe, Co, Ni, Pd | Continuous titration | 7, 38, 76 |
| | Direct injection | 7, 38 |
| | Semi-adiabatic flow | 74 |
| | Not specified | 76 |
| Lanthanides; Ce, Gd | Continuous titration | 38, 74 |
| | Incremental titration | 38 |
| | Direct injection | 38 |
| Actinides; U, Th | Continuous titration | 38, 74 |
| | Direct injection | 38 |
| Endpoints by large heat of dilution effects | Continuous titration | 68, 72, 73, 77 |
| Endpoints using coupled reactions when $\Delta H$ is small | Continuous titration | 1 |
| Endpoints using flow enthalpimetry | Flow | 72 |
| Endpoints using thermochemical indicators | Continuous titration | 38, 68, 72–74, 76–78 |
| Esters | Direct injection | 68 |
| Ethers | Not specified | 68 |

TABLE 2 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| Gases ($CO_2$, $SO_2$, $NO_2$, $N_2O_4$) | Direct injection | 9 |
| Inorganic acids and bases by neutralization, solvent: aqueous | Isoperibol cont. titr. | 38, 74, 79 |
| | Isoperibol incremental | 38 |
| | Direct injection | 38 |
| | Semi-adiabatic flow | 74 |
| | Flow | 38 |
| | Not specified | 73 |
| solvent: non-aqueous | Continuous titration | 38, 74 |
| | Not specified | 73 |
| Metals and ligands by complexation, solvent: aqueous | Isoperibol cont. titr. | 38, 76, 80 |
| | Continuous titration | 38, 74, 76 |
| | Isoperibol dir. inject. | 38, 76 |
| | Semi-adiabatic flow | 74 |
| | Flow | 76 |
| | Not specified | 73, 76 |
| solvent: non-aqueous | Continuous titration | 74 |
| Nitriles | Flow | 68 |
| Olefins, acetylenes and aromatic compounds | Isoperibol titration | 68 |
| | Isoperibol dir. inject. | 9, 77, 81 |
| Organic acids and bases by neutralization, solvent: aqueous | Isoperibol cont. titr. | 74 |
| | Continuous titration | 68, 79 |
| | Semi-adiabatic flow | 74 |
| | Flow | 68 |
| | Not specified | 73 |
| solvent: non-aqueous | Continuous titration | 68, 74, 77 |
| | Direct injection | 68 |
| | Not specified | 73 |
| Organometallic compounds, solvent: non-aqueous | Continuous titration | 38, 74, 77 |
| Pharmaceutical compounds | Continuous titration | 7, 68, 74 |
| | Not specified | 73 |
| Polyethers and polyesters | Isoperibol dir. inject. | 7 |
| Reaction stoichiometry | Continuous titration | 74 |
| Secondary processes which take place at a catalyst surface | Not specified | 82 |
| Species by precipitation reactions, solvent aqueous | Isoperibol cont. titr. | 74, 78 |
| | Continuous titration | 38 |
| | Isoperibol dir. inject. | 78 |
| | Not specified | 73 |
| solvent: non-aqueous | Isoperibol cont. titr. | 78 |
| | Continuous titration | 38, 68 |

TABLE 2 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| Species by redox reactions, solvent: aqueous | Isoperibol cont. titr. | 71, 74 |
| | Continuous titration | 38, 74, 83 |
| | Direct injection | 38 |
| | Not specified | 73, 83 |
| Sugars | Isoperibol dir. inject. | 9 |
| Surface-active materials for preferential adsorption for industrial applications | Semi-adiabatic flow | 84 |
| Surface areas of particles ($m^2$ $g^{-1}$) and particle size from heat of adsorption data (quality control) | Semi-adiabatic flow | 84, 85 |
| Surfactants | Continuous titration | 68 |
| Thermograms | Isoperibol cont. titr. | 72, 75 |
| Thio-acids, thio-ethers and disulfides | Continuous titration | 68 |
| Very small amounts of materials that exhibit catalytic activity (kinetic titration) | Continuous titration | 1 |
| | Not specified | 1, 72 |
| Water in organic liquids and solids | Titration | 38 |
| | Isoperibol dir. inject. | 38, 77 |
| | Direct injection | 9, 38, 77 |
| | Semi-adiabatic flow | 7 |
| | Flow | 77 |
| | Batch | 38 |
| | Not specified | 74 |
| Water of hydration in salts | Isoperibol dir. inject. | 9 |
| B. *Enthalpy change*, $\Delta H$, *determinations* | | |
| Catalysts (activation energy) | DSC | 67 |
| | Types other than DSC | 67 |
| Cation exchange reactions in clays | Isoperibol cont. titr. | 69 |
| Dilution | Titration | 72 |
| | Flow | 24, 86, 87 |
| | Batch | 73, 87 |
| Hydrogen bonding | Flow | 87 |
| | Batch | 87 |
| Hydrolysis reactions | Flow | 88 |
| Inorganic and organic acid–base neutralization reactions solvent: aqueous | Continuous titration | 38, 68, 79 |
| | Flow | 88 |
| | Many types used but specific type is not mentioned | 89 |
| | Not specified | 79 |
| solvent: non-aqueous | Continuous titration | 38, 68 |
| | Many types used but | 89 |

TABLE 2 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| | specific type is not mentioned | |
| | Not specified | 79 |
| Interactions between pre-adsorbed species and gaseous reactants (heterogeneously catalyzed reaction) | Not specified | 67, 82 |
| Metal–ligand complexation reactions, solvent: aqueous and non-aqueous | Continuous titration | 38, 76 |
| | Direct injection | 38, 76 |
| | Flow | 38, 76 |
| | Batch | 8, 38 |
| | Many types used but specific types not mentioned | 90 |
| Mixing of two or more solvents | Isothermal cont. titr. | 1, 91 |
| | Isoperibol cont. titr. | 91 |
| | Incremental | 92 |
| | Isothermal displacement | 91 |
| | Isoperibol dir. inject. | 91 |
| | Isothermal flow | 70, 91, 92 |
| | Heat cond. flow | 91 |
| | Semi-adiabatic flow | 72, 91 |
| | Isoperibol batch | 91 |
| | Isothermal batch | 91 |
| | Heat cond. batch | 91 |
| | Adiabatic batch | 91 |
| Precipitation reactions, solvent: aqueous | Isoperibol cont. titr. | 38, 78 |
| Reactions from calorimetric data | Continuous titration | 22, 75, 93 |
| | Flow | 22 |
| | Not specified | 22 |
| Redox reactions, solvent: aqueous | Continuous titration | 38, 83 |
| Small batteries under load and no-load conditions | Heat cond. batch | 94–96 |
| Solution of a gas in a liquid | Isothermal gas inject. | 97 |
| Solution of a liquid in a liquid | Titration | 72 |
| | Isoperibol batch | 3, 86 |
| Solution of a solid in a liquid | Isothermal batch | 24 |
| | Isoperibol batch | 24, 86 |
| Surface adsorption of gases by solids | Isoperibol adsorption | 82 |
| | Isothermal adsorption | 82 |
| | Heat cond. adsorption | 82 |
| | Flow adsorption | 84 |
| | Adiabatic adsorption | 82 |

TABLE 2 (continued)

| Determination | Method [a] | Basic references |
|---|---|---|
| Surface adsorption of liquids by solids | Semi-adiabatic flow | 84 |
| | Isothermal batch | 70 |
| | Heat cond. batch | 85 |
| Surface adsorption of solutes from solution by solids | Heat cond. batch | 98 |
| C. *Equilibrium constant,* K, *determinations* | | |
| Enantiomeric recognition | Isoperibol cont. titr. | 99 |
| Hydrogen bonding | Flow | 87 |
| | Batch | 87 |
| Metal–ligand complexes | Continuous titration | 69, 74, 76 |
| | Not specified | 76 |
| Organic and inorganic acids and bases | Isoperibol cont. titr. | 38, 68, 74 |
| | Titration | 68, 74 |
| Reactions from calorimetric data | Continuous titration | 73, 74, 93 |
| | Not specified | 22, 75 |
| D. *Kinetic parameter determinations* | | |
| Reactions involving catalysts | Heat conduction | 67, 82 |
| | Not specified | 67, 82 |
| Reactions not involving catalysts | Isoperibol dir. inject. | 24, 39 |
| | Heat conduction flow | 3, 24, 59 |
| | Semi-adiabatic flow | 72, 88 |
| | Flow | 22 |
| | Heat cond. batch | 3 |

[a] Abbreviations are defined in Table 1 footnote.

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