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The High-temperature Microcalorimetry of Inorganic Substances

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The essential features of high-temperature microcalorimetry have been described, and the possibilities provided by its use in various fields such as inorganic chemistry, mineralogy, power engineering, etc. have been demonstrated. The procedures of high-temperature microcalorimetry have been classified according to the types of process studied: solution, oxidation, hydrogenation, dissociation, phase transformations, the mixing of melts, etc., and illustrated for substances with different compositions and uses: metals, oxides, salts, synthetic and natural compounds, and minerals. The results of the studies have been compared with data obtained by calorimetry involving solution in aqueous solutions and by combustion calorimetry. The bibliography contains 423 references.

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I. INTRODUCTION

Heat-conducting calorimeters,[1] the theory and practice of which were developed by Tian[2] and Calvet,[3-9] have been called microcalorimeters, because of their high sensitivity in the measurement of the heats of various reactions and physical transformations. The name indicates that it is possible to measure very small quantities of heat (microcalories) using specimens with different masses and dimensions. Microcalorimeters are usually classified as instruments for low (90–500 K), medium (273–700 K), and high (273 to 2100 K) temperatures. The present review deals chiefly with microcalorimeters for high temperatures (273–1800 K), and the possibilities provided by their use in chemistry, mineralogy, the production of ceramics, metallurgy, and other fields. The types of microcalorimeter indicated do not differ fundamentally from one another. The main differences are in the construction of the working thermostats (blocks), where the detector cells surrounded by the thermojunctions are placed; in the materials from which they are made; and also in the construction of the apparatus for initiating the reactions. The heat losess from a high-temperature calorimter increase in proportion to T^4; in practice, this means that the loss of heat at 1000 K will be eight times greater,

and that at 1500 K 27 times greater, than that at 500 K. The fact that it is impossible to eliminate these losses makes it difficult to use more accurate adiabatic and other calorimeters at high temperatures (1050–1600 K).[10,11]

The design of high-temperature microcalorimeters (HTMC) makes it possible, instead of eliminating the heat losses from the working cells, to achieve their practically complete compensation during the experiment. Thus in spite of the lower accuracy of the measurements compared with the above-mentioned calorimeters, HTMC have the advantages of simplicity, convenience in use, and reliability of the measurements in long experiments at high temperatures (1000–1800 K). A high-temperature microcalorimeter is a universal heat-measuring instrument, which can be used to determine the enthalpies of various chemical reactions, physical transformations, and phase transformations (fusion, volatilisation, adsorption, mixing of solutions, polymorphic transformations, order–disorder transformations, etc.). Compared with other calorimeters, HTMC make it possible to study heterogeneous reactions and not only to determine the quantity of heat liberated or absorbed but also simultaneously to study the kinetics of the process. These and a number of other advantages have led to the extensive application of high-temperature microcalorimetry in chemistry,[12–16] mineralogy,[17–22] metallurgy,[23–30], the study of the thermodynamics of solid solutions (order–disorder transformations),[31,32] etc. HTMC are now also used to study the thermochemistry of salt and metallic systems used to accumulate solar energy and ground heat.[33–36]

II. ESSENTIAL FEATURES OF THE METHOD AND APPARATUS

High-temperature microcalorimeters (1300 K) appeared in 1955–1966[37–39] after the development of the theory of heat-conducting calorimeters[40–42] and the construction of electronic regulators for maintaining high temperatures in the block with a high accuracy.[43–45] The design of the Setaram Calvet high-temperature microcalorimeter (1000 °C) is shown in Fig. 1. The actual microcalorimeter consists of two calorimeter cells placed symmetrically in cylindrical holes in a massive block made of stainless steel[46] or fused alumina.[47] A battery of Pt–PtRh (13%) thermocouples (396 junctions) is placed between the outer surface of each detector cell and the cylindrical surface of the hole in the block. The batteries of the two cells are connected according to a differential scheme. Some of the thermocouples can be used to generate the Peltier effect in the detector cells.[4,48,49]

A slight change in the temperature of the block produces identical heat fluxes to the two cells, and identical EMF's are produced in the thermo-batteries, and as a result of the differential connection they compensate one another. A change in temperature in one of the cells produces an EMF which is proportional to the intensity of the heat flux from this detector cell to the block (or conversely). This EMF is amplified and recorded graphically using a recorder. The area bounded by the heat-liberation curve and the zero line, which is proportional to the heat of the process being studied, is measured using planimeters, electronic integrators, or computers.[50,51] The form of the curve defines the thermal power of the process at each moment of time, so that its kinetics can be studied.[52–54] The instrument is calibrated to determine its basic constants, that is its sensitivity and time constant.[4,8] The geometric form of the specimen and the degree of filling of the cell influence the nature of the curve, and may introduce errors into the time constant of the instrument.[55,56]

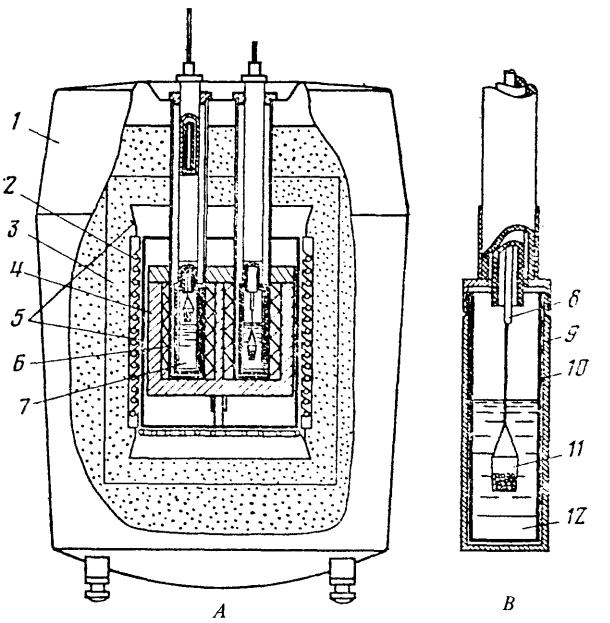


Figure 1. *A*) Calvet microcalorimeter; *1*) calorimeter casing, *2*) heater, *3*) furnace, *4*) massive block, *5*) metal screens, *6*) thermocouples, *7*) calorimetric cell; *B*) calorimetric cell: *8*) ceramic rod, *9*) metal cell casing, *10*) platinum beaker, *11*) platinum crucible, *12*) solvent melt.

The constants of the microcalorimeter are determined experimentally by various methods: by electrical calibration from the Joule effect, by placing an ohmic resistance in the detector cell;[57] by measuring the known heats of fusion or solution of standard chemical compounds;[25,58,59] from the known heats of chemical reactions;[60–64] and by mixing† standard substances for which the temperature changes in enthalpy are known. The calibration using the Joule effect can also be carried out without an ohmic resistance, by using the resistance of the thermocouples surrounding the detector cell (Peltier effect); when calibration from the Peltier effect is used, there is no heat flux along the leads.[49,65] Electrical calibration from the Joule effect has not been widely used in high-temperature microcalorimetry. HTMC are mainly calibrated by mixing, that is the basic constants of the instrument are determined from the change in the heat content of standard specimens of Pt, Au, or Al_2O_3, which after being brought to constant temperature at 298 K are dropped into the working cell of the microcalorimeter, heated to the required temperature.[66,67] The mixing method is used to calibrate calorimeters which are to be used to measure high-temperature enthalpies or to measure the enthalpies of solution of metals and compounds in various solvent melts. In a number of procedures, additional apparatus is introduced into the cells, for example to initiate chemical reaction. The possibility of introducing various pieces of equipment into the working cells (ampoules, manipulators, initiating assemblies, stirrers) represents the main advantage of HTMC over the other types of calorimeter.

† Other terms are encountered in the literature: the dump method, drop calorimetry.

Methods involving the programming and complete automation of the calorimetric experiment have been widely used in recent years.[68-70]

Large high-temperature microcalorimeters. Extensive development of high-temperature microcalorimetry took place after the foundation, in 1957, of the Institut de Microcalorimetrie et de Thermogenese de Marseille,[71] in whose workshops the first high-temperature microcalorimeters (1300 K) were constructed;[46] using their pattern, the firm of Setaram in Lyons began the mass production of instruments with the following technical characteristics: temperature range 300–1300 K, heating rate 0.5–60 K h^{-1}, sensitivity 2.5 mJ mW^{-1} or 4 μV mW^{-1}, time constant 120–130 s (1100 K); dimensions of the working cells: diameter 17 mm, height 80 mm, volume 15 cm^3; parameters of the HTMC: height 100 cm, diameter 60 cm, mass 300 kg. This HTMC (1300 K) belongs to the class of large microcalorimeters, and as a result of its temperature stability under isothermal conditions it can be used to carry out long experiments (weeks or months). Large high-temperature microcalorimeters (1300 K) have been used mainly to study the thermochemistry of metals and metallic alloys.[40,55,72-75] Assemblies making it possible to carry out experiments in air or in an inert medium and in a vacuum, depending on the aims of the study of solid–liquid metallic systems, have been developed.[74-86]

To increase the sensitivity and improve the reproducibility of the results in the measurement of the heat content and the determination of the heat capacity of solids, a special working cell was used,[19] with a partition and a semi-automatic device for dropping the specimen into the cell.[87,88] A simple procedure for determining the heats of fusion and solution involves dropping the solid specimen (298 K) into the liquid situated in the working cell of the calorimeter at the given temperature[27,28,88] (Fig. 2*a*). A disadvantage of this method is that the thermal effect of the process being recorded consists of two effects: an endothermic effect due to the change in the enthalpy of the solid substance, and the thermal effect of the solution of the solid in the liquid. The two effects are superimposed on one another, and their separation in the integration of the areas under the curves is difficult and leads to large errors, which are difficult to take into account.[17] Much better results in the determination of heats of solution are obtained when the solid is suspended in a small dish at a short distance from the liquid, and dropped into the liquid after temperature equilibrium has been reached, for example by opening a clamping mechanism, controlled from outside the apparatus (Fig. 2*b*).[80] Very reliable and accurate results are obtained by the "indirect drop" procedure. The solid specimen, at room temperature, is dropped into a graphite ampoule situated above the melt, and brought to the same temperature as the melt in the calorimeter (Fig. 2*c*). When temperature equilibrium has been reached, the solid specimen is lowered by means of a manipulator into the liquid for the measurement of the enthalpy of solution. The procedure can be carried out in a vacuum and in an inert atmosphere.

In the study of the enthalpies of mixing of molten salts, one of the salts in a sealed quartz ampoule is lowered into the working cell containing a melt of the other salt. When temperature equilibrium has been reached, the ampoule is broken by a manipulator, and the enthalpy of mixing of the melts or the solution of the solid salt in the melt is measured (Fig. 2*d*).[89-92] To determine the enthalpies of solution of small specimens, a special device to start the reaction was constructed for use with Setaram HTMC.[71] To prevent corrosion, the device was made of a ceramic oxide (Al_2O_3) and a heat resistant alloy which did not form a scale up to 1600 K. The successful microcalorimetric study of metals and alloys led to the development, in various laboratores, of specieal HTMC (1500 K and 1880 K) for studying the partial enthalpies of the reaction of oxygen with nonstoichiometric oxides of iron, uranium, zirconium, etc. In these instruments, as a result of the intensive radiative transfer of heat, direct contact between the thermocouples and the wall of the cell or block is not necessary. The calibration is carried out from the known enthalpies of oxidation of thorium by oxygen.[93-98] HTMC (1000 K) with graphite or platinum cells in which it is possible to carry out experiments in a vacuum have been constructed to study the enthalpies of solution of metals in liquid aluminium and tin[99,100] and to measure the enthalpies of mixing of liquid metals with sulphur and selenium.[101]

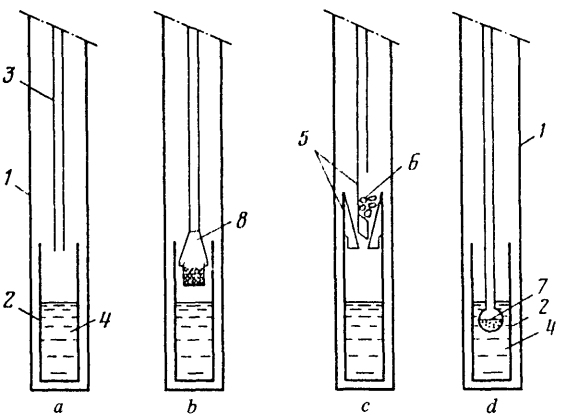


Figure 2. Types of reaction assembly placed in the calorimeter to measure the enthalpies of solution in melts: *1*) cell casing, *2*) platinum reaction vessel, *3*) directing tube, *4*) solvent melt, *5*) graphite specimen holder for heating to the temperature of the solvent and for dropping it, *6*) specimen, *7*) ampoule containing the specimen, *8*) holding clamp for heating the specimen to the temperature of the solvent and for dropping it.

In 1955, Kleppa (USA) constructed a high-temperature heat-conducting microcalorimeter with one working cell, designed for the study of the solution of metals at 800 K,[37] and in the period 1960–1966 he developed HTMC with two working cells,[12,38,102,103] designed for the study of the solution of oxides and silicates in oxide melts, selected for the first time for these purposes in another study.[104] In a subsequent model, the Chromel/Alumel thermojunctions were replaced by Pt–PtRh (13%) thermojunctions, and the HTMC were calibrated by mixing using platinum and gold specimens. Kleppa was the first to use an original device for initiating solution, placed symmetrically in both cells. An HTMC operating up to 1100 K with a quartz device for "starting" the reaction was constructed[105] for determining the enthalpies of solution of solid inorganic compounds in melts with the composition $3Na_2O.4MoO_3$ by Navrotsky's method.

High-temperature microcalorimeters with a small number of thermocouples. Heat-conducting calorimeters with a limiting working temperature of up to 1800 K have recently been developed. The blocks of these calorimeters are made of molybdenum and have smaller dimensions; some workers[106,107]

have used planar PtRh (6%)–PtRh (30%) or WRh (5%)–WRh (10%) thermo-batteries with a smaller number of thermocouples, placed in an aperture in the side of the working cell. This HTMC is designed to operate in air and in a vacuum at 800–1800 K.[108,109] Another type of calorimeter, manufactured by Setaram, differs from the HTMC (1300 K) produced by the same firm in that both calorimeter cells of fused Al_2O_3 are arranged in it vertically and coaxially one above the other (Fig.3). The detector cells, the thermo-battery, and the device for circulating argon and for cooling with water are placed in a vertical heater with a large uniform temperature zone; the temperature of the heater can be raised to 2000 K. The procedure for carrying out measurements with this apparatus in the study of metals and metallic systems has been described,[110–113] but its possibilities have not been fully studied. In the next type of heat-conducting microcalorimeter, in contrast to the Tian–Calvet microcalorimeter, the junctions of the thermo-batteries were connected in series.[114,115] This HTMC can operate in the temperature range 298–1500 K or 103–900 K under programmed heating conditions in a vacuum or in a medium of inert gases. A heat-conducting microcalorimeter of spherical shape, in which the liquid components, in a sealed quartz ampoule, are mixed by rotating the calorimeter through 180° has been constructed for determining the heats of mixing of volatile, solid, and liquid salts. The HTMC is calibrated from the Joule effect using a calibration resistance, and the uncertainty of the determination of the enthalpies of mixing is 4%.[116]

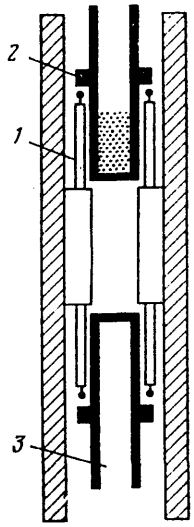


Figure 3. Diagram of the vertical arrangement of the cells in the HTMC (1800 K): *1*) thermocouple, *2*) reaction assembly with the melt, *3*) empty cell.

Heat-conducting calorimeters of the DTA type. Heat-conducting microcalorimeters fitted with a temperature controller for maintaining a stable rate of heating (or cooling) while preserving the advantages of HTMC are acquiring the additional functions of instruments for quantitative thermal analysis. It is difficult, however, to carry out experiments under programmed heating conditions using large HTMC (1300 K) with a large number of thermojunctions, with a large time constant. The heating rate should be low (0.5 to 8 K h^{-1}), or stability of the zero line is not achieved. The long time required to carry out the experiment, and the need to decrease the senstivity of the instrument, make large HTMC unsuitable for experiments under constant heating conditions, although the possibility does exist (for determining large thermal effects, for example on fusion).[39,64,90,95,117,118]

In the USSR, one of the first microcalorimeters for studying the rates of heterogeneous solid–gas reactions and dissociation at 770 K was constructed in the Chemistry Department of Moscow State University.[119] A microcalorimeter designed for the study of heat capacities, phase transformations, the ageing of metals, etc., operating at 400–1100 K, has been described[120]. A differential microcalorimeter, constructed[121] in accordance with the Calvet principle and operating in the range 300–1000 K, is designed mainly for quantitative thermal analysis; it is calibrated electrically, has an accuracy of 3–5%, and the mass of the specimen is 0.6–6 g.

Microcalorimeters designed to operate under conditions of heating and cooling (1–20 K min^{-1}) are called "scanning calorimeters". The Setaram differential scanning microcalorimeter (DSC) combines the accuracy and sensitivity of the traditional HTMC with the speed of carrying out the experiments characteristic of DTA.[122,123] This DSC operates in the range 150–1000 K under isothermal and scanning conditions; the operation of the instrument is controlled by a computer, and the time constant of the detector is 12 s.

III. ENTHALPIES OF SOLUTION OF INORGANIC COMPOUNDS

In many calorimetric procedures, enthalpies of solution provide a basis for determining enthalpies of formation, which are fundamental thermochemical characteristics used in chemistry, mineralogy, metallurgy, power engineering, etc.[124–135] Various refractory compounds and minerals are insoluble in acids, however, even at high temperatures (298–353 K). The calorimetric study of solution in aqueous solutions of acids is therefore unsuitable for determinining the enthalpies of formation of refractory compounds or minerals. A much more effective method than acid calorimetry is provided by high-temperature solution microcalorimetry, where a liquid melt, having considerable solvent power at 1000–1200 K, is used instead of an aqueous acid solution. The procedure for carrying out the measurements was developed in 1960 [38] after the development of a high-temperature Tian–Calvet microcalorimeter with a special quartz device for studying the solution of specimens with a mass of 50–300 mg.[12,37] This procedure is used to determine the enthalpy change in the solution of a weighed specimen of a solid in a liquid solvent consisting of a melt with a definite composition.

A similar device for solution, made of a refractory ceramic and a heat-resistant alloy, has been described.[66] An advantage of this device is that it is possible to work with small specimens of the substances being studied, so that rare materials can be investigated (toxins, synthetic compounds, cosmic minerals). The enthalpies of solution in melts are generally about one tenth of the enthalpies of solution in aqueous acid solutions. This means that although the uncertainty of the determination of the enthalpy of solution in HTMC is ~1%,[18,52,136] whereas that for calorimetry involving solution in acids is ~0.1%, the uncertainty of the enthalpy of formation of a substance being studied will be the same in both cases (Table 1). The main advantage of the HMTC method for studying solution is that it is possible to measure the enthalpies of solution of refractory compounds

(oxides, chromites, ferrites, silicates, aluminosilicates, etc.) using specimens with a mass of 5–30 mg. A limitation of the method must be mentioned, however, namely the difficulty of studying hydrated compounds, including natural and synthetic minerals. Procedures for studying solution in melts have been examined in detail.[9,12,17,18,51,66,136–141]

Table 1. Comparative characteristics of calorimetric methods for determining the enthalpies of formation of silicates.[20,53]

Characteristics of the method	Calorimetry involving solution in acids (HF etc.)	High-temperature microcalorimetry involving solution in melts
Principle of the method	adiabatic calorimeter	Calvet microcalorimeter
Working temperature range, K	289–398 (depending on the type of calorimeter)	298–1800 (depending on the type of calorimeter)
Mass of specimen for one experiment	500–2000 mg	5–300 mg
Example of an experimentally determined quantity: $(\Delta H_T^0)_{solution(\alpha\text{-}SiO_2)}$, kcal mole^{-1}	−33.0±0.02	−1.01±0.05
Uncertainty of the determination (attainable) of $(\Delta H_T^0)_{solution}$, %	0.1	1
Uncertainty of the calculated enthalpy of formation of the silicate (ΔH_f^0), kcal mole^{-1}	0.1–0.2	0.1–0.2
Influence of dilution and change in the concentration of the solution on the value of ΔH_T^0, solution	considerable	slight
Solubility of the most important oxides (Al_2O_3, Cr_2O_3, MgO, SiO_2, etc.)	satisfactory or poor	good (at 1000–1300 K)
Work with hydrated compounds	possible	difficult

1. Oxide Solvents

As in classical solution calorimetry,[142] the main problem in the thermochemical study of the solution of substances in melts is the choice of the solvent melt. Up to the present, in spite of the accumulation of knowledge on the physical chemistry of melts and the equilibrium diagrams obtained, there is no scientifically based criterion for selecting a solvent melt in relation to the composition of the compounds being studied. The main requirements which must be satisfied in the choice of a solvent can be formulated as follows.

1. With allowance for the existing temperature limit of the measurements in the high-temperature microcalorimetric procedure, the melting point of the solvent should be comparatively low (900–1200 K), and the vapour pressure should be so low that the enthalpy of volatilisation does not distort the measurements being made.

2. The solvent should have a buffer capacity, that is it should have a concentration range in which the enthalpy of solution is practically independent of the composition of the solvent.

3. The solvent should be stable in the atmosphere in which the measurements are being made.

The most important characteristic of the solvent melt is its acid–base behaviour; the magnitude and sign of the enthalpy of solution are determined by the degree of acidic or basic character of the solvent.[12] The scale of basic strength of oxide solvent melts can be interpreted as a series of states of the oxygen ion between O^{2-} and O^- as a result of polarisation in the presence of metal cations.[143] The equilibrium for the acid–base behaviour in an oxide melt can then be written in the form:

$$\text{acid} + O^{2-} \rightarrow \text{base}$$

The greater the activity of the oxygen ion, the greater the basic strength of the melt.[144–146] For example, in the Na_2O–MoO_3 system, sodium oxide is a strongly basic oxide (base), and MoO_3 is a strongly acidic oxide (acid). Thus the solution of MoO_3 in melt rich in sodium oxide can be represented as the following chain of equilibria:

$$O^{2-}(\text{liquid}) + MoO_3(\text{crystalline}) \rightarrow MoO_4^{2-}(\text{liquid})$$
$$MoO_4^{2-}(\text{liquid}) + MoO_3(\text{crystalline}) \rightarrow Mo_2O_7^{2-}(\text{liquid})$$
$$MoO_3(\text{crystalline}) \rightarrow MoO_3(\text{liquid})$$

Solvents based on oxides, so-called oxide solvents, have been most widely used in high-temperature microcalorimetry. The possibility of using an oxide solvent (V_2O_5) to dissolve the oxides of a number of metals at 958 ± 5 K and lead vanadates at 953 K was first demonstrated by Yokokawa and Kleppa.[147,148] V_2O_5 was not used in other studies, since it does not show acid–base properties. The efforts of research workers were subsequently directed to the search for melts combining acidic and basic properties, since only these melts can fulfil the functions of a calorimetric solvent and give an acid–base equilibrium. The equilibrium diagram of the PbO–B_2O_3 system[149–151] showed a range of compositions (17–67% B_2O_3) existing in the liquid state at 973 K; a buffer capacity was detected for the composition $2PbO.B_2O_3$, and this was found to be suitable for dissolving many oxides (SiO_2, GeO_2, Fe_2O_3).[152] A less widely used melt for these oxides has the composition $9PbO.3CdO.4B_2O_3$, from the ternary PbO–CdO–B_2O_3 system.[153,154]

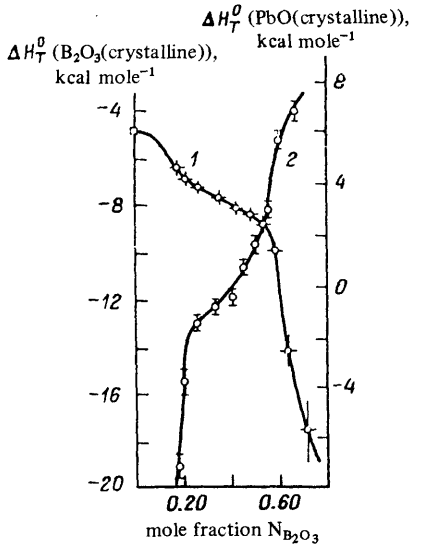


Figure 4. Dependence of the enthalpy of solution of PbO (*1*) and B_2O_3 (*2*) on the mole fraction of B_2O_3 in a PbO–B_2O_3 melt at 1173 K; *N* is the mole fraction.

The composition ranges of the PbO–B_2O_3 system corresponding to a buffer capacity of the solvent can be seen from Fig. 4, but oxides such as TiO_2, SnO_2, NiO, and their compounds are insoluble in these solvents. A so-called molybdate melt with the composition $3Na_2O.4MoO_3$ (75% Na_2MoO_4–25% MoO_3) (Fig. 5) has been proposed for these oxides;[155] because of its appreciable volatility, this melt is unsuitable at temperatures above 700 °C, and is unstable in

a reducing medium. A study of the acid–base properties of the K_2MoO_4–MoO_3 system[156] established that in the composition range 35–80 mole % MoO_3, this system has a lower melting point than Na_2MoO_4–MoO_3, and compositions with 40–50 mole % MoO_3 can be used as a calorimetric solvent at 820 K (Fig. 6).

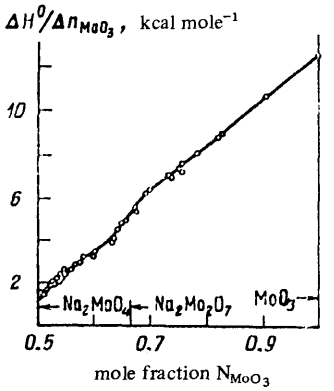


Figure 5. Dependence of the enthalpy of solution of MoO_3 on the mole fraction of MoO_3 (N_{MoO_3}) in an Na_2O–MoO_3 melt.

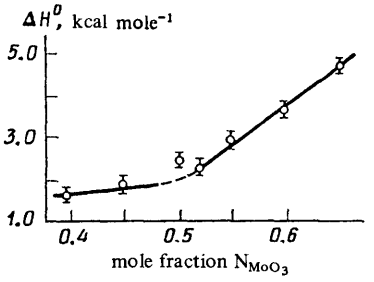


Figure 6. Dependence of the enthalpy of solution of MoO_3 on the mole fraction (N) of MoO_3 in a K_2O–MoO_3 melt.

To find new calorimetric solvents, the following oxide systems have been studied: PbO–SiO_2 at 1173 K,[157] PbO–GeO_2 at 1173 K,[158] Li_2O–B_2O_3 at 1213 K, and Na_2O–B_2O_3 at 1258 K.[159] A solvent with the composition 0.5 $LiBO_2$–0.5 $NaBO_2$, liquid at 940 K, was detected.[159] The ternary eutectic mixture with the composition Na_2O–B_2O_3–SiO_2, liquid at 1973 K, is a good solvent for dissolving SiO_2, Al_2O_3, MgO, CaO, FeO, and MnO in a reducing medium. This composition is hygroscopic, however, and this introduces a number of difficulties in its preparation and storage. Buffer properties have been detected for various compositions of the Na_2O–P_2O_5 system.[160] In the range 56–61 mole % Na_2O, the phosphates are liquid at 1116 K, and are of undoubted interest as promising calorimetric solvents. Up to the present, however, the phosphate melt has not found extensive application in high-temperature microcalorimetry. The main characteristics of the widely used and new solvent melts are summarised in Table 2. The practically unlimited possibilities in the further search for solvent melts are opening up extensive opportunities for using high-temperature microcalorimetry to study various classes of inorganic substance.

Table 2. Compositions and ranges of application of solvent melts used in high-temperature solution microcalorimetry.[17,20,249]

Composition of melt	Range of application K	Used to dissolve	Notes
$2PbO·B_2O_3$ or $9PbO·3CdO·4B_2O_3$ *	920–1170	SiO_2, GeO_2, Fe_2O_3, Cr_2O_3, MgO, CaO, NiO, CuO, ZnO, CdO, Cu_2O	not suitable for dissolving TiO_2, SnO_2, Mn_2O_3
$3Na_2O·4MoO_3$	870–1020	TiO_2, SnO_2, Mn_2O_3, MgO, CaO, NiO, ZnO, CdO Ln_2O_3	acidic oxides and SiO_2 do not dissolve well; volatile at T > 970 K
$0.35Na_2O·0.35B_2O_3·0.3SiO_2$	1070–1170	SiO_2, Al_2O_3, MgO, CaO, FeO **, MnO **	hygroscopic (special storage conditions)
$0.5Li_2O·0.5Na_2O·B_2O_3$ ($LiBO_2$+$NaBO_2$)	940	WO_3, FeO, MnO	new solvent, procedures not developed
$2.5Na_2O·1.5P_2O_5$ ($NaPO_3$+$Na_4P_2O_7$)	1120	WO_3	ditto

*Solvent with narrower range of application.
**A reducing medium is required.

2. Minerals and Silicate Systems

The enthalpies of formation of minerals are used for thermodynamic calculations when modelling the processes involved in natural and synthetic mineral formation.[161,162] High-temperature solution microcalorimetry has been developed for refractory natural and synthetic minerals.

Al_2O_3–SiO_2 system. The enthalpy of solution of the oxide Al_2O_3 was determined for the first time in 1964,[153,163] after which the enthalpies of solution of polymorphic forms of the compound Al_2SiO_5—the minerals andalusite, kyanite, sillimanite and mullite—in the ternary solvent $9PbO.3CdO.4B_2O_3$ at 968 ± 2 K was determined.[164,165] The calculated enthalpies of formation and other thermochemical constants (entropy, heat capacity) were used to construct the p–T diagram of the Al_2O_3–SiO_2 system over a wide range of temperatures and pressures.[166] Additional studies of the enthalpies of solution of minerals with the composition Al_2SiO_5 in molten $2PbO.B_2O_3$ at 974 + 2 K [167,168,169] made it possible to refine the p–T diagram, so that the coordinates of the triple point of the Al_2O_3–SiO_2 system coincided with published data.[170–173]

The measured enthalpies of solution of different forms of SiO_2 (quartz, cristobalite, coesite, stishovite, glass) in moltent $9PbO.3CdO.4B_2O_3$ at 970 ± 2 K, and the high-temperature enthalpies determined by mixing, were used to construct the p–T diagram giving the stability of the coesite–stishovite system, to calculate the thermodynamics of the polymorphic transformation[86] and the high-temperature equilibria for the forms of SiO_2, and to reach conclusions important for geology and seismology.[174] For sillimanite it was established that there is a difference in the enthalpies of solution of specimens[175] kept at different temperatures before the experiments (influence of the degree of ordering of the structure).

MgO–Al_2O_3–SiO_2 system. The stability fields of the solid phases in the MgO–Al_2O_3–SiO_2 system are usually studied using apparatus for high and superhigh pressures and temperatures.[176,177] The technical difficulties and the time

required for this experimental method, and the lack of published thermochemical data for the thermodynamic analysis of the stability fields of the solid phases on the $p-T$ diagrams, led to the development of the thermochemical study of the minerals in molten $2PbO.B_2O_3$ at 1000–1300 K [178–181] (Tables 3 and 4). The enthalpies of formation and heat capacities calculated in this way, and the known entropy values, can be used to carry out calculations for many reactions which are models for processes taking place in the earth's crust and upper mantle and used in silicate technology. The differences observed in the enthalpies of solution of natural compounds and their synthetic analogues indicate that the data obtained for a synthetic system cannot be transferred uncritically to a natural system, even when the compositions of the phases are similar.

Table 3. Enthalpies of solution of oxides in high-temperature solvents based on boric oxide (ΔH_T^0, kcal mole^{-1}).

Oxide	T, K	ΔH_T^0	Refs.	T, K	ΔH_T^0	Refs.
	$9PbO\cdot3CdO\cdot4B_2O_3$			$2PbO\cdot B_2O_3$		
α-Al_2O_3	978	7.6±0.2	[153]	965	7.88±0.24	[180]
α-Al_2O_3	—	—	—	1173	7.47±0.13	[180]
α-Al_2O_3	—	—	—	970	7.73±0.08	[179]
β-Al_2O_3	978	2.3	[164]	—	—	—
δ-Al_2O_3	978	5±3	[164]	—	—	—
Al_2O_3	978	4.6	[164]	—	—	—
SiO_2	943	−3.64±0.07[a]	[165]	943	−1.02±0.05	[197,404]
SiO_2	970	−3.1±0.1[b]	[86]	965	−1.04±0.07[a]	[180]
SiO_2	970	−2.8±0.1[c]	[86]	1173	1.03±0.05[a]	[180]
SiO_2	970	−3.5±0.1[d]	[86]	970	−1.23±0.07[a]	[179]
SiO_2	970	−3.8±0.1[e]	[86]	986	−0.76±0.10[a]	[205]
SiO_2	970	−3.5±0.1[f]	[86]	973	−1.01±0.05[a]	[185]
SiO_2	970	−4.45±0.15[g]	[86]	1070	0.19±0.05[a]	[185]
SiO_2	970	−4.5±0.1[i]	[86]	—	—	—
MgO	965	−2.19±0.16	[197]	965	0.72±0.03[h]	[180]
MgO	970	−2.19±0.16	[222]	1173	2.01±0.54[h]	[180]
MgO	970	−8.86±0.07[j]	[222]	1173	1.99±0.11[h]	[185]
MgO	958	−9.4±0.6[k]	[147]	970	1.18±0.08[h]	[179]
MgO	—	—	—	986	1.39±0.17[h]	[205]
MgO	—	—	—	1070	1.68±0.23[h]	[185]
MgO	—	—	—	1170	2.1±0.4[h]	[185]
MgO	—	—	—	955	−1.8±0.8	[197]
CaO	958	−32.7±0.7[k]	[147]	936	−13.05±0.22	[205]
CaO	—	—	—	970	−13.18±0.39	[137]
CaO	—	—	—	973	−13.30±0.07	[185]
CaO	—	—	—	967	−15.08±0.17	[187]

Notes: [a] quartz; [b] quartz; [c] quartz-2; [d] cristobalite; [e] coesite-1; [f] coesite-2; [g] stishovite; [h] periclase; [i] vitreous; [j] solvent $3Na_2O.4MoO_3$; [k] solvent V_2O_5.

Measurement of the enthalpies of solution of magnesium silicates and aluminates in molten $2PbO.B_2O_3$ at 973 K [180] and $MgAl_2O_4$ in $9PbO.3CdO.4B_2O_3$ [181,182] showed that the solution of MgO takes place slowly and is not quantitative at 973 K, and is characterised by two thermal effects: a large exothermic effect is first observed, followed by a small endothermic effect. This two-stage solution was attributed[181] to the formation of an intermediate compound (exothermic effect), followed by its solution (endothermic effect). At 1173 K the solution of MgO is complete and takes place at a high rate, and the exothermic effect almost disappears;[183–186] the results of the determination of the enthalpy of formation of magnesium silicate show good agreement with the data obtained by calorimetry involving solution in acids (see Table 11 below). Thus the study of magnesium

Table 4. Enthalpies of solution [$(\Delta H_T^0)_{solution}$, kcal mole^{-1}] of silicates in molten $2PbO.B_2O_3$ and enthalpies of formation from the oxides (ΔH_f^0, kcal mole^{-1}); the number of experiments is given in brackets.

Compound	T, K	$(\Delta H_T^0)_{solution}$	$-\Delta H_f^0$	Refs.
Al_2SiO_5 (sillimanite)	974	6.93±0.01(8)	—	[167]
Al_2SiO_5 Isillimanite)	963	7.11±0.29(11)	—	[175]
Al_2SiO_5 (sillimanite)	970	6.92±0.09(11)	0.57±0.14	[179]
Al_2SiO_5 (sillimanite-II)	970	7.07±0.09(11)	—	[179]
Al_2SiO_5 (kyanite)	974	8.35±0.17(15)	—	[167]
Al_2SiO_5 (kyanite)	973	8.38±0.23(6)	—	[193]
Al_2SiO_5 (kyanite)	973	8.42±0.11(12)	—	[397]
Al_2SiO_5 (andalusite)	973	8.01±0.30(3)	—	[193]
Al_2SiO_5 (andalusite)	973	7.42±0.15(10)	—	[397]
Al_2SiO_5 (andalusite-I)	974	7.55±0.19(10)	0.71±0.30	[168]
Al_2SiO_5 (andalusite-II)	974	7.62±0.21(24)	—	[168]
$Mg_2Al_4Si_5O_{18}$ (cordierite)	963	28.1±1.5(8)	16.1±0.7	[181]
$Mg_2Al_4Si_5O_{18}$ (cordierite, vitreous)	963	25.9±1.3(5)	—	[181]
$Mg_2Al_4Si_5O_{18}$ (cordierite)	967	30.04±0.86(6)	—	[178]
$Mg_2Al_4Si_5O_{18}$ (cordierite)	970	27.54±0.22(8)	15.87±0.31	[179]
$Mg_2Al_4Si_5O_{18}$ (cordierite, synthetic 1.0% FeO)	970	27.95±0.42(6)	16.28±0.48	[179]
$MgSiO_3$ (enstatite)	967	8.95±0.33(7)	—	[177]
$MgSiO_3$ (enstatite)	967	8.4±1.9(4)	—	[180]
$MgSiO_3$ (enstatite)	970	8.78±0.13(24)	8.81±0.47	[179]
$Mg_{0.9}Al_{0.2}Si_{0.9}O_3$ (enstatite)	970	7.74±0.11(9)	7.01±0.15	[179]
$MgSiO_3$ (enstatite)	965	8.36±0.19(13)	8.68±0.21	[180]
$MgSiO_3$ (enstatite)	1173	11.19±0.15(7)	8.15±0.57	[180]
$Mg_2Si_2O_6$ (enstatite)	970	17.20±0.21(5)	—	[198]
$MgSiO_3$ (clinoenstatite)	1170	18.28±0.19(12)	8.36±0.27	[187]
$Al_2SiO_4F_2$ (topaz, fluoride)	970	—	21.96±0.85	[407]
$Mg_2Al_4SiO_{10}$ (sapphirine)	967	21.78±3.15(6)	48.95±3.23	[128]
$Mg_2Al_4SiO_{10}$ (sapphirine, 1.7% FeO)	970	20.02±1.22(12)	45.88±1.25	[179]
Mg_2SiO_4 (forsterite)	970	16.11±0.24(23)	14.97±0.27	[179]
Mg_2SiO_4 (forsterite)	965	15.84±0.13(7)	15.44±0.05	[180]
Mg_2SiO_4 (forsterite)	1173	19.91±0.33(6)	14.88±0.83	[180]
Mg_2SiO_4 (forsterite)	1170	19.22±0.19	14.30±0.33	[184]
$Mg_3Al_2Si_3O_{12}$ (pyrope, synthetic)	970	27.79±0.32(18)	20.21±0.38	[137]
$Mg_3Al_2Si_3O_{12}$ (pyrope)	970	27.73±0.28(5)	—	[199]
$Mg_3Al_2Si_3O_{12}$ (pyrope)	973	16.7±6(7)	—	[191,192]
$Ca_3Al_2Si_3O_{12}$ (grossular)	973	42.5±5(8)	—	[191,192]
$Ca_3Al_2Si_3O_{12}$ (grossular)	970	42.2±0.4(7)	—	[199]
$Ca_3Al_2Si_3O_{12}$ (grossular)	970	42.41±0.4(11)	77.91±0.6	[137]
$Ca_3Fe_2Si_3O_{12}$ (andradite-I)	975	51.1(6)	—	[191,192]
$Ca_3Fe_2Si_3O_{12}$ (andradite-II)	975	51.6(3)	—	[191,192]
$Ca_2Al_2SiO_7$ (gehlenite)	970	—	30.64±0.31	[395]
$CaMgSi_2O_6$ (diopside)	970	20.53±0.75(17)	—	[199]
$CaAl_2SiO_6$ (oligoclase)	970	11.5±0.2(9)	—	[199]
$CaAl_2SiO_6$ (oligoclase)	970	11.55±0.23	18.23±0.29	[137]
$Ca_2MgSi_2O_7$ (akermanite)	970	—	42.92±0.72	[395]
$CaMgSi_2O_6$ (diopside, synthetic)	970	20.38±0.21(6)	—	[198]
$CaMgSi_2O_6$ (diopside)	970	20.53±0.25(17)	34.99±0.41	[137]
$CaMgSi_2O_6$ (diopside)	975	20.38±0.37(10)	—	[184,185]
$MgCaSi_2O_6$ (diopside, vitreous)	1170	23.46±0.34(8)	33.35±0.47	[184,185]
$MgCaSi_2O_6$ (diopside, natural)	986	20.95±0.25(13)	34.3±0.4	[205]
$MgCaSi_2O_6$ (diopside, synthetic)	986	20.82±0.28(8)	—	[205]
$MgCaSi_2O_6$ (diopside)	986	20.90±0.26(21)	—	[205]
$MgCaSi_2O_6$ (diopside, vitreous)	986	0.111±0.085(7)	—	[205]
$CaSiO_3$ (wollastonite, synthetic)	970	7.01±0.22(5)	—	[137]
$CaSiO_3$ (wollastonite, synthetic homogeneous)	970	7.07±0.20(14)	21.48±0.36	[137]
$CaSiO_3$ (wollastonite, high-pressure phase)	970	5.43±0.15(5)	19.84±0.34	[137]
$NaAlSi_3O_8$ (albite)	970	5.23±0.23	—	[208]
$KAlSi_3O_8$ (orthoclase)	970	10.06±0.58	—	[208]
$CaSiO_3$ (pseudo-wollastonite)	970	5.51±0.06(7)	19.92±0.31	[137]
$CaSiO_3$ (wollastonite)	973	6.96±0.29(8)	21.48±0.39	[184]
$CaSiO_3$ (wollastonite-I)	1170	9.13±0.31(8)	—	[184]
$CaSiO_3$ (wollastonite-II)	1070	7.76±0.73	—	[184]
$CaSiO_3$ (pseudo-wollastonite)	973	5.70±0.10(12)	—	[184]
$CaAl_2SiO_8$ (anorthite, synthetic)	970	15.2±0.3(38)	23.14±0.45	[137]
$CaAl_2SiO_8$ (anorthite, natural)	970	16.02±0.36(16)	23.93±0.48	[137]
$CoCaSi_2O_6$	986	17.51±0.33(10)	26.7±0.5	[205]
$NiCaSi_2O_6$	986	21.08±0.33(9)	27.0±0.5	[205]
Mn_2SiO_4	986	14.20±0.20(4)	12.2±0.3	[205]
$MnSiO_3$ (rhodonite)	986	6.98±0.26(6)	6.3±0.3	[205]
$MnSiO_3$ (pyroxyoptite)	986	6.92±0.19(6)	—	[205]
$MnSiO_3$ (rhodonite)	986	6.95±0.22(12)	—	[205]
Ni_2SiO_4 (olivine structure)	986	19.86±0.93(5)	—	[254]
Ni_2SiO_4 (spinel)	986	18.43±0.57(7)	—	[254]
α-Co_2SiO_4	986	15.49±0.17(7)	—	[206]
β-Co_2SiO_4	986	13.34±0.35(4)	—	[206]
γ-Co_2SiO_4	986	12.80±0.25(3)	—	[206]
$CoSiO_3$	986	6.92±0.23(5)	—	[206]
α-Fe_2SiO_4	986	3.74±0.13(6)	—	[206]
γ-Fe_2SiO_4	986	3.04±0.15(4)	—	[206]
$FeSiO_3$	986	13.70±0.07(5)	—	[206]
$MgAl_2O_4$ (spinel, synthetic)	970	14.29±0.14(5)	5.38±0.18	[199]
$MgAl_2O_4$ (spinel)	965	14.51±0.51(19)	5.93±0.56	[180]
$MgAl_2O_4$ (spinel)	960	14.81±0.37(6)	5.33±0.67	[180]
Al_2SiO_5[a] (sillimanite)	968	5.47±0.01(7)	—	[166]
Al_2SiO_5[a] (andalusite)	968	5.95±0.10(4)	—	[166]
Al_2SiO_5[a] (kyanite)	968	6.33	—	[165]
Al_2SiO_5[a] (mullite)	968	10.08±0.10(5)	—	[166]
$MgAl_2O_4$[b]	970	14.13±0.22	8.72±0.29	[222,182]

Notes. [a] solvent $9PbO.3CdO.4B_2O_3$; [b] solvent $3Na_2O.4MoO_3$.

compounds in melts must be carried out at temperatures not lower than 1173 K.[136,187] Measurement of the enthalpies of solution of sapphirine in $2PbO.B_2O_3$ at 973 K showed the influence of temperature on the stability of natural ordered and synthetic disordered sapphirines.[188,189]

$CaO-MgO-Al_2O_3-SiO_2$ system. The enthalpies of formation of the solid phases of this system, determined from the enthalpies of solution in molten $2PbO.B_2O_3$ at 970 K, have been determined[137,190] (see Tables 4 and 5). The dependence of the values obtained for the enthalpy of solution on the size of the anorthite specimen was determined;[155] no significant change in the enthalpies of solution was observed for specimens weighing 43.72–34.90 mg. The enthalpy of solution of natural garnets (grossular, andradite, and pyrope) in molten $2PbO.B_2O_3$ at 973 K has been determined experimentally.[191] The phase relationships for pyrope and minerals of granulite and eclogite facies have been examined by the Schreinemakers method on coordinates $p-T$.[192,193] The thermochemical data for grossular $Ca_3Al_2(SiO_4)_3$, andradite $Ca_3Fe_2(SiO_4)_3$, and uvarovite $Ca_3Cr_2(SiO_4)_3$ have been analysed, and the most reliable experimental data on the $p-T$ equilibria have been used to calculate the Gibbs free energy.[194]

The thermochemical properties of the most important phases of the $CaO-MgO-SiO_2$ system have also been studied[195] by high-temperature solution microcalorimetry in molten $2PbO.B_2O_3$ at 1000–1300 K,[183,184] and the properties of $MgSiO_3$ have been studied at 965 ± 2 K in two solvents: $2PbO.B_2O_3$ and $9PbO.3CdO.4B_2O_3$ (Table 4).

New data on the enthalpy of the $\alpha \rightarrow \beta$ phase transformation of $CaSiO_3$ have been obtained from the enthalpies of solution of the two phases in molten $2PbO.B_2O_3$ at 973 K.[196] Improvements in the experimental technique for high-temperature solution microcalorimetry[137,198,199] made it possible to increase the accuracy of the determination of the enthalpies of solution of the phases and solid solutions of the $CaO-MgO-SiO_2-Al_2O_3$ system. Thus for a number of minerals of this system, synthesised at high temperatures and pressures, the enthalpies of solution of the extreme members in $2PbO.B_2O_3$ (970 K) have been determined, and the results have been used to study the thermochemistry of the solid solutions.[198–201]

The enthalpies of solution in $2PbO.B_2O_3$ (970 K) of the extreme members of the olivine system Mg_2SiO_4 (forsterite)–Fe_2SiO_4 (fayalite) made it possible to study a model of the molecular activity of silicate minerals#, of considerable importance for carrying out calculations for natural systems.[202–204] The determination of the enthalpies of solution in $2PbO.B_2O_3$ (1036 K) of minerals of the pyroxene group ($MgCaSi_2O_6$, $NiCaSi_2O_6$, $MnSiO_3$) and the enthalpies of fusion of $CaMgSi_2O_6$ (diopside) and $CaMgSi_2O_6$ (diopside glass),[205] and also the enthalpies of solution of cobalt silicates (α-Co_2SiO_4, β-Co_2SiO_4, γ-Co_2SiO_4), synthesised at a high pressure, made it possible to construct the $p-T$ diagrams for SiO_2-MO silicate systems.[206] The thermochemistry of the glasses and solid and liquid phases in the systems $CaMgSi_2O_6$–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$, SiO_2–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$, SiO_2–Al_2O_3–CaO–Na_2O, and $NaAlSi_3O_8$–$KAlSi_3O_8$ [determination of

Table 5. Enthalpies of solution of oxides (ΔH^0_T, kcal mole^{-1}) in high-temperature solvents based on B_2O_3, MoO_3, and V_2O_5.

Oxide	T, K	ΔH^0_T	Refs.	T, K	ΔH^0_T	Refs.	T, K	ΔH^0_T	Refs.
	$9PbO\cdot3CdO\cdot4B_2O_3$			$2PbO\cdot B_2O_3$			$3Na_2O\cdot4MoO_3$		
BeO	98	3.45±0.2	[237]	—	—	—	958	1.0±0.3[a]	[147]
SrO	—	—	—	967	−25.41±0.02	[221]	958	−47.9±0.9[a]	[147]
BaO	—	—	—	967	−31.00±0.02	[221]	958	−61.7±0.6[a]	[147]
ZnO	970	4.26±0.12	[222]	970	4.28±0.20	[197]	970	−3.2±0.6	[222]
ZnO	—	—	—	1173	4.86±0.05	[183]	—	—	—
CdO	970	2.71±0.03	[222]	1173	2.98±0.06	[183]	970	−9.59±0.07	[222]
CdO	958	−15.9±0.6[a]	[147]	967	2.53±0.05	[221]	—	—	—
CdO	970	5.72±0.15	[222]	970	5.95±0.15	[197]	970	−4.90±0.09	[222]
CoO	—	—	—	986	5.38±0.26	[210]	958	−6.4±0.4[a]	[147]
CoO	—	—	—	973	5.66±0.19	[228]	—	—	—
NiO	970	9.96±0.18	[222]	970	8.66±0.18	[197]	970	−0.77±0.07	[222]
NiO	—	—	—	986	8.56±0.35	[205]	958	−10.6±0.7[a]	[147]
NiO	—	—	—	1173	10.94±0.12	[183]	—	—	—
CuO	970	9.14±0.09	[222]	986	8.52±0.27	[227]	970	2.65±0.05	[222]
CuO	—	—	—	1173	12.41±0.10	[183]	958	4.3±0.7[a]	[147]
Fe_2O_3	970	16.72± 0.11	[222]	973	18.04±0.45	[225]	970	−0.49±0.05	[222]
Fe_2O_3	—	—	—	974	16.68±0.12	[216]	974	−0.41±0.02	[216]
Ga_2O_3	970	8.07±0.15	[222]	974	7.50±0.09	[216]	974	5.86±0.09	[216]
In_2O_3	—	—	—	—	—	—	974	−17.83±0.14	[216]
Cr_2O_3	—	—	—	1173	5.35±0.08	[183]	—	—	—
TiO_2	—	—	—	971	3.53±0.10[i]	[219]	943	2.38±0.09[g]	[222,180]
Fe_2O_3	970	16.7±0.11	[222]	973	18.04±0.45	[225]	970	−0.49±0.05	[222]
Ga_2O_3	970	8.07±0.15	[222]	—	—	—	—	—	—
Cr_2O_3	—	—	—	1173	5.35±0.08	[183]	—	—	—
PbO	1073	3.5±0.2	[152]	967	4.15±0.06	[223]	953	−18.42±0.33[a]	[147]
GeO_2	970	−6.22±0.11	[222]	970	−4.70±0.16	[197]	—	—	—
GeO_2	966	0.5±0.2[d]	—	967	0.50±0.07	[221]	—	—	—
GeO_2	966	−8.4±0.5[b]	—	986	−4.96±0.17	[227]	—	—	—
B_2O_3	—	—	—	973	9.97±0.12	[228]	974	7.91±0.02	[216]
CuO_2	—	—	—	1173	18.80±0.18	[183]	—	—	—
Mn_2O_2	—	—	—	—	—	—	970	16.56±0.15	[222]
WO_3	1116	(3.81±3.53)[c]	[160]	973	−14.07±0.14	[224]	970	7.24±0.18	[154]
MoO_3	—	—	—	—	—	—	973	2.47±0.07	[244]

Notes. [a] solvent V_2O_5; [b] quartz structure; [c] solvent $2.5Na_2O.1.5P_2O_5$, mole fraction $N_{Na_2O} = 0.5–0.61$; [d] solvent $2PbO.B_2O_3$, tetragonal structure; [e] solvent $2PbO.B_2O_3$, hexagonal structure; [f] solvent $2PbO.B_2O_3$, vitreous; [g] rutile; [h] solvent $0.5LiBO_2 + 0.5NaBO_2$; [i] solvent $3Na_2O.4MoO_3$.

The enthalpies of formation of the solid solutions of the Mg_2SiO_4–Fe_2SiO_4 system were studied by measuring the enthalpies of solution in molten $LiBO_2$–$NaBO_2$ in a medium of argon at 1180 K.[220]

the enthalpies of solution in $2PbO.B_2O_3$ (970 K, 986 K) and the heat content $H_T - H_{298}$ (mixing in HTMC)] has been studied.[140,207,208] The results obtained were used to carry out a thermodynamic study of models of the phase equilibria for the liquid surfaces of the ternary systems and general models of the structures of geological magma.[209,210,211,212]

The extensive accumulation of material on the high-temperature microcalorimetry of silicate and oxide systems has made it possible to distinguish the corresponding mineral associates of practical importance in geochemistry, petrology, geothermometry, and silicate technology.[213,214,215,216,217] The use of thermochemical data to construct $p-T$ diagrams has been reviewed.[218] At present, high-temperature solution microcalorimetry is used to study "dry" systems. The problem of the study of hydrated chemical compounds (minerals) is at an initial stage of development. Thus an attempt has been made[219] to measure the enthalpies of aqueous solutions at a pressure of 2 kbar and 1073 K by a combined method involving high-temperature microcalorimetry and the use of high-pressure ampoules. The difficulties in studies of this kind are associated with various technical problems in the construction of the calorimetric apparatus.

3. Chemical Compounds

A second direction taken by studies in high-temperature solution microcalorimetry arose in connection with the need to determine the thermochemical characteristics of refractory substances,[197,213,221,229] which cannot be studied by other thermochemical methods. From the methodological viewpoint, the two directions, that is the thermochemistry of minerals and the thermochemistry of inorganic substances, represent a single whole, since they use similar procedures (the same measurement temperature, solvent composition, thermochemical cycle, etc.), and the materials studied as models of minerals are often products of the chemical industry. The difference between these two directions is determined only by the purposes of the studies.

Since the separate aims of the thermochemistry of inorganic substances are fairly varied, the results of the studies have been systematised in the present work on the basis of the method of study used. The main problem in the development of a procedure is the choice of solvent, in which the enthalpy of formation is determined by measuring the enthalpies of solution of the compound being studied and its components under identical conditions (solvent composition, temperature of the experiment, and concentration of dissolved substances). For example, for complex oxides (chromites, silicates, tungstates, molybdates, gallates, manganates, aluminates, ferrites, etc.), the thermochemical cycle is as follows:

$$MWO_4(\text{crystalline}) + (\text{solvent}) \rightarrow M^{2+}(\text{liquid}) + WO_4^{2-}(\text{liquid}) + (\Delta H_T^0)_1 \quad (1)$$

$$MO(\text{crystalline}) + WO_3(\text{crystalline}) + (\text{solvent}) \rightarrow M^{2+}(\text{liquid}) + WO_4^{2-}(\text{liquid}) + (\Delta H_T^0)_2 \quad (2)$$

$$MO(\text{crystalline}) + WO_3(\text{crystalline}) \rightarrow MWO_4(\text{crystalline}) + (\Delta H_T^0)_2 - (\Delta H_T^0)_1 \quad (3)$$

The known values of the enthalpies of formation of the oxides and the values obtained for $(\Delta H_T^0)_1$ and $(\Delta H_T^0)_2$ are used to calculate the enthalpy of formation of the compound. A similar procedure is used in the study of the thermochemistry of solid solutions or isomorphous mixtures, but instead of oxide mixtures [reaction (2)], a mixture of the compounds forming the required solid solution is used.[224]

Vanadium(V) oxide (V_2O_5). Kleppa[225] used molten vanadium(V) oxide as a solvent to measure the enthalpies of solution of PbO and lead vanadates with the compositions $Pb_2V_2O_7$, $Pb_3(VO_4)_2$, and $Pb_8V_2O_{13}$ at 953 K to determine the enthalpies of formation of the vanadates from the oxides. The enthalpies of solution of the oxides of the alkaline earth metals and various transition metals were measured in the samel solvent[147] at 958 ± 5 K (Tables 3 and 5).

Table 6. Enthalpies of solution of oxides (ΔH_T^0, kcal mole^{-1}) in high-temperature solvents based on B_2O_3 and MoO_3.

Oxide	ΔH_{975}^0	ΔH_{973}^0 [242, 244]	ΔH_{974}^0 [216]	ΔH_{1075}^0 [216]
	$2PbO \cdot B_2O_3$	$3Na_2O \cdot 4MoO_3$	$3Na_2O \cdot 4MoO_3$	
La_2O_3	−4.82±0.01[a]	−75.4±1.8	−81.5±0.6	−62.1±0.4
Nd_2O_3	−3.30±0.13[a]	−81.1±1.0	—	−60.3±0.3
Sm_2O_3	−3.5±0.01[a]	−75.3±1.2	−73.6±0.2	−59.9±0.4
Eu_2O_3	33.37±0.44[c]	−50.5±0.7	—	—
Gd_2O_3	−3.68±0.03[a]	−70.2±1.0	−49.3±0.4	−49.5±0.7
Dy_2O_3	−9.92±0.32[b]	−48.6±0.5	—	—
Ho_2O_3	−14.09±0.29[b]	−44.4±1.0	—	—
Er_2O_3	—	−44.9±0.5	−46.1±0.2	—
Tu_2O_3	−17.84±0.03[b]	—	−45.1±0.3	—
Yb_2O_3	—	−41.1±0.5	−42.5±0.4	−38.7±0.3
Lu_2O_3	−10.87±0.09[b]	−37.2±0.8	—	—
Y_2O_3	4.95±0.44[c]	−53.0±0.6	—	43.8±0.1
Sc_2O_3	—	−32.2±0.8	—	31.4±0.1
Pr_6O_{11}	—	−129.2±1.0	—	—
Ce_2O_3	—	—	−32.5±0.4	—

Notes: [a]mixture of $0.5Ln_2O_3 + 0.5Al_2O_3$; [b]mixture of $1.5Ln_2O_3 + 2.5Al_2O_3$;[234] [c]mixture of $0.5Ln_2O_3 + 0.5Fe_2O_3$.[231,232]

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 7. Enthalpies of solution of compounds in high-temperature solvents based on B_2O_3 and MoO_3 (ΔH_T^0, kcal mole^{-1}).

Compound	ΔH_{970}^0	Refs.	Compound	T, K	ΔH_T^0	Refs.
	$3Na_2O \cdot 4MoO_3$			$2PbO \cdot B_2O_3$		
$MgMnO_4$	10.42±0.15	[222]	$MgCr_2O_4$	1173	18.48±0.1	[183]
$CoMn_2O_4$	15.44±0.12	[222]	$NiCr_2O_4$	1173	17.56±0.13	[183]
$NiMn_2O_4$	15.31±0.08	[222]	$CuCr_2O_4$	1173	15.26±0.22	[183]
$CuMn_2O_4$	16.17±0.18	[222]	$ZnCr_2O_4$	1173	25.25±0.12	[183]
$ZnMn_2O_4$	19.92±0.17	[222]	$CdCr_2O_4$	1173	18.42±0.14	[183]
$CdMn_2N_4$	14.46±0.05	[222]	Ca_2SiO_4	967	4.40±0.29	[221]
Mg_2TiO_4	−9.32±0.11	[222]	Sr_2SiO_4	967	−1.96±0.19	[221]
Co_2TiO_4	−1.38±0.11	[222]	Ba_2SiO_4	967	0.33±0.05	[221]
Zn_2TiO_4	−3.19±0.10	[222]	Cd_2SiO_4	967	12.95±0.12	[221]
$ZnNiTiO_4$	2.00±0.17	[222]	Be_2SiO_4[c]	970	7.95±0.15	[237]
$ZnCoTiO_4$	0.0±0.2	[222]	Mg_2SiO_4	965	10.2±0.2	[197]
$MgWO_4$	16.07±0.25	[154]	Pb_2SiO_4	967	11.45±0.04	[223]
$CoWO_4$	16.74±0.11	[154]	Pb_4SiO_6	967	18.57±0.25	[223]
$NiWO_4$	17.04±0.22	[154]	$PbSiO_3$	967	7.55±0.09	[223]
$CuWO_4$	16.52±0.20	[154]	Ca_2GeO_4	967	2.87±0.24	[221]
$ZnWO_4$	14.11±0.17	[154]	Sr_2GeO_4	967	−11.59±0.31	[221]
$CoWO_4$	16.58±0.05	[154]	Ba_2GeO_4	967	−5.95±0.12	[221]
Fe_2TiO_5[a]	−0.10±0.10	[240]	Cd_2GeO_4	967	14.60±0.17	[221]
α-$CdTiO_3$[a]	−0.6±0.1	[257]	$CuGeO_3$	986	8.82±0.22	[227]
β-$CdTiO_3$[a]	−4.17±0.15	[257]	$Co_3B_2O_6$	973	26.48±0.19	[228]
$Mg_3B_2O_6$[b]	16.56±0.21	[248]	$Co_2B_2O_5$	973	16.82±0.11	[228]
$Mg_2B_2O_5$[b]	23.85±0.33	[248]	CoB_4O_7	973	−9.32±0.26	[228]
MgB_4O_7[b]	31.9±1.0	[248]	$CoGeO_4$	965	21.5±0.3	[197]
—	—	—	$NaAlO_2$	975	4.70±0.11	[236]
—	—	—	$KAlO_3$	975	−0.07±0.12	[236]
—	—	—	Na_2CO_3	975	31.84±0.25	[236]
—	—	—	K_2CO_3	975	29.36±0.25	[236]

Notes: [a]T = 965 K; [b]T = 973 K; [c]solvent $9PbO.3CdO.4B_2O_3$.

A solvent melt with the composition $2PbO.B_2O_3$ was proposed by Kleppa[152] for the study of the enthalpies of solution of MgO, α-Al_2O_3, and $MgAl_2O_4$, and has since been widely used (Tables 5–9). The enthalpies of formation of magnesium silicates and aluminates at 973 K and 1173 K [180] and of magnesium, nickel, copper, zinc, and cadmium chromites with the composition MCr_2O_4 at 1173 ± 2 K,[183] determined from the measured enthalpies of solution of the compounds and the original oxides, have been used to study the thermodynamic and crystal-chemical characteristics of the formation of chromite spinels[226] and the acid–base properties of transition metal oxides.

Table 8. Enthalpies of solution of compounds in high-temperature solvents based on B_2O_3 and V_2O_5 (ΔH^0_T, kcal mole^{-1}).

Compound	ΔH^0_{970}	Refs.	Compound	T, K	ΔH^0_T	Refs.
	$9PbO\cdot 3CdO\cdot 4B_2O_3$			V_2O_5		
$BeAl_2O_4$	15.05±0.15		$Pb_2V_2O_7$	953	9.91±0.33	[148]
$BeAl_6O_{10}$	23.35±0.23	[237]	$Pb_3V_2O_8$	953	−1.75±0.63	[148]
$ZnAl_2O_4$	22.42±0.26	[237]	$Pb_8V_2O_{13}$	953	−92.9±4.4	[148]
$CdAl_2O_4$	5.82±0.17	[222]	$CaMgB_2O_5$[a]	973	18.42±0.44	[401]
$CuAl_2O_4$	11.57±0.14	[222]	$CaWO_4$[c]	973	12.54±0.16	[400]
$CoAl_2O_4$	22.22±0.14	[222]	$MnWO_4$[c]	940	39.55÷47.92	[250]
$NiAl_2O_4$	18.30±0.15	[222]	$FeWO_4$[c]	940	31.24÷42.28	[250]
$ZnFeAlO_4$	22.8±0.2	[222]	$Fe_{0.5}Mn_{0.5}WO_4$[c]	940	40.5÷45.1	[250]
$MgGa_2O_4$	15.49±0.17	[222]	$MgGeO_4$[b]	970	11.31±0.30	[197]
$ZnGa_2O_4$	20.78±0.13	[222]	$MgGeO_3$[b]	970	5.31±0.19	[197]
$CdGa_2O_4$	12.60±0.12	[222]	$CoGeO_4$[b]	965	21.5±0.3	[197]
$CuGa_2O_4$	13.25±0.22	[222]	$CoGeO_3$[b]	965	8.65±0.21	[197]
$CoGa_2O_4$	21.32±0.15	[222]	Zn_2GeO_4	965	14.65±0.30	[197]
$NiGa_2O_4$	18.95±0.15	[222]	Co_2SiO_4	965	16.02±0.3	[197]
$MgFe_2O_4$	19.46±0.14	[222]	Zn_2SiO_4	965	15.37±0.40	[197]
$CoFe_2O_4$	28.33±0.09	[222]	Ni_2SiO_4	965	19.64±0.38	[197]
$NiFe_2O_4$	27.90±0.09	[222]	—	—	—	—
$CuFe_2O_4$	20.81±0.14	[222]	—	—	—	—
$ZnFe_2O_4$	23.63±0.16	[222]	—	—	—	—
$CdFe_2O_4$	17.66±0.17	[222]	—	—	—	—
Co_3GeO_4	19.28±0.33	[222]	—	—	—	—
Ni_2GeO_4	23.22±0.33	[222]	—	—	—	—

Notes: [a]solvent $2PbO.B_2O_3$; [b]solvent $9PbO.3CdO.4B_2O_3$; [c]solvent $0.51LiBO_2 + 0.5NaBO_2$, mole fraction of tungstate 0.00345–0.0258 and 0.0012–0.0252 respectively.

The energy characteristics and stability of the structures of silicates and germanates of the transition metals (Co, Ni, Zn) and magnesium,[197] the alkaline earth metals (Ca, Sr, Ba) and cadmium,[221] and minerals based on them have been studied by measuring the enthalpies of solution of the silicates, germanates, and corresponding oxides at (965–967) ± 2 K. A lead borate solvent has been used successfully by a number of authors to study the thermochemistry of the phases formed in the systems $PbO–SiO_2$ ($PbSiO_3$, Pb_2SiO_4, Pb_4SiO_6),[223] $CuO–GeO_2$ ($CuGeO_3$),[227] and $CoO–B_2O_3$ ($Co_3B_2O_6$, $Co_2B_2O_5$, CoB_4O_7)[228] in the thermochemistry of solid solutions.[140,224,229]

The thermochemistry of ferrites, borates, aluminates, and gallates with the composition§ $LnMoO_3$ (Ln represents a lanthanide, yttrium, or scandium) at 974, 975, and 1075 K [216,230–233] and aluminates[234,235] with the compositions $LnAlO_3$ and $Ln_3Al_5O_{12}$ at 875 K has been studied by measuring the enthalpies of solution of the compounds and the corresponding oxides of the lanthanides, iron, boron, aluminium, and gallium. The enthalpies of solution of sodium and potassium aluminates and carbonates at 975 K have been used to determine the enthalpies of formation of $NaAlO_2$ and $KAlO_2$.[236]

§ In the compounds $LnMO_3$. M represents Fe, B, Al, or Ga.

Table 9. Enthalpies of solution of compounds of the lanthanides in melts based on B_2O_3 or MoO_3 [216,230,234,244,245,246,243] (ΔH^0_T, kcal mole^{-1}).

Ln	$LnAlO_3$[b], (975 K)	$Ln_2(MoO_4)_3$[a], (973 K)	$NaLn(MoO_4)_2$[a], (973 K)	$LnBO_3$[a] (974 K)	$LnGaO_3$ or (Ln_2FeO_4)(974 K)
La	9.50±0.20	−0.26±0.14	21.6±0.4	7.34±0.05	−20.6±0.2[a]
La	−15.40±0.07[c]	—	—	—	(−19.10±0.17[c])
Pr	—	8.81±0.34	18.3±0.7	—	—
Nd	8.03±0.72	9.71±0.47	17.4±0.5	9.34±0.12[b]	1.05±0.07[b]
Nd	−14.22±0.12[c]	—	—	—	(4.78±0.07[b])
Sm	7.29±0.15	12.81±0.18	17.3±0.7	5.2±0.2[c,e]	(−16.47±0.05)[c]
Sm	−10.68±0.05[c]	—	—	9.01±0.07[b,e]	—
Eu	—	3.20±0.10	19.3±0.5	10.40±0.05[b]	(29.77±0.11[b])
Gd	5.31±0.12	16.20±0.88	16.9±0.4	7.4±0.2	—
Gd[e]	—	20.70±1.36	—	—	—
Tb	—	—	—	7.07±0.02[b]	—
Dy	32.22±0.35[d]	3.05±0.15	17.0±0.8	10.35±0.07[b]	—
Ho	34.58±0.22[d]	2.86±0.25	20.0±0.5	10.49±0.12[b]	—
Er	—	21.4±1.1	20.2±0.6	4.04±0.05	—
Yb	—	15.71±0.82	18.8±0.5	6.43±0.07[c]	—
Lu	32.71±0.14[d]	14.7±0.5	20.4±0.4	4.64±0.07[b]	—
Y	7.62±0.09	19.79±0.64	19.0±0.5	11.21±0.07[b]	(−16.30±0.14[c])
Tu	41.07±0.43	—	—	4.67±0.20	—
Sc	−15.4±0.07[c]	7.23±0.17	2.2±0.3	4.06±0.10[b]	(−14.84±0.12)[c]
Ce	1.23±0.02[a]	—	—	15.4±0.2	2.99±0.02[a]

Notes: [a]solvent $3Na_2O.4MoO_3$; [b]solvent $2PbO.B_2O_3$; T = 974 K or 975 K; [c]solvent $3Na_2O.4MoO_3$; T = 1075 K; [d]aluminate with the composition $Ln_3Al_5O_{12}$; [e]forms of $LnBO_3$ or $Gd_2(MoO_4)_3$.

Molten $9PbO.3CdO.4B_2O_3$. Beryllium aluminates and silicate (and also BeO, Al_2O_3, SiO_2) dissolve more readily in a melt with the composition $9PbO.3CdO.4B_2O_3$.[237] This solvent was therefore used[197] to refine the results of the study of the solution of MgO and various metal silicates and germanates, and also for a thermochemical study of the aluminates, ferrites, gallates, and germanates of bi- and tervalent metals.[222]

Molten $3Na_2O.4MoO_3$. A number of solvent melts based on MoO_3 are known.[139,155,156,238,239] The most widely encountered is the melt with the composition $3Na_2O.4MoO_3$, first used by Navrotsky and Kleppa.[155] The enthalpies of solution of simple and complex oxides of the transition metals in this melt were measured in a cycle of studies to determine the enthalpies of formation of the titanates M_2TiO_4 [222,240] and manganates M_2MnO_4 [222] with the spinel structure, and the isostructural tungstates MWO_4;[154,241] the thermodynamic data were compared with the mechanism of spinel formation by the titanates and manganates, and the thermodynamic characteristics of the tungstates were compared with the data for the sulphates, carbonates, and silicates of the same metals.

A systematic study of the thermochemistry of lanthanide molybdates has been carried out.[242–247] The enthalpies of formation of simple and double lanthanide molybdates were determined for the first time by measuring the enthalpies of solution of the oxides Ln_2O_3, Pr_6O_{11}, and MoO_3 and the molybdates $Ln_2(MoO_4)_3$, and $NaLn(MoO_4)_2$, and Na_2MoO_4 at 973 ± 0.5 K and of $Na_4La(MoO_4)_4$ at 897 K. The enthalpies of formation of magnesium borates were determined[248] from data on the composition of the compounds formed in the $MgO–B_2O_3$ system and the enthalpies of solution of the

borates $Mg_3B_2O_6$, $Mg_2B_2O_5$, and MgB_4O_7 and the oxides MgO and B_2O_3, measured at 973 ± 2 K.

Molten $NaPO_3$–$Na_4P_2O_7$. A relatively new solvent melt with the composition $2.5Na_2O.1.5P_2O_5$, proposed by Ko and Kleppa,[160] has been used to measure the enthalpies of solution of WO_3 in the presence of Na_2O (1116 K). There are no published data on other studies with this solvent.

Molten $LiBO_2$–$NaBO_2$. The enthalpies of formation of the solid solutions formed by manganese and iron tungstates have been determined[249,250] by measuring the enthalpies of solution of the solid solutions and oxides of tungsten(VI), iron(II), and manganese(II) in a solvent with the composition $0.5LiBO_2 + 0.5NaBO_2$ at 940 K¶.

Molten KCl–LiCl. A eutectic melt of lithium and potassium chlorides has been used[251] to measure the enthalpies of solution of the double chlorides of caesium and the transition metals (and calcium) at 728 K, to determine the enthalpies of formation (Table 9) and to study the stability of the ions in the melts. The enthalpy of the reaction of lead oxide (PbO) with liquid cadmium in the working cell at 800 K, measured by mixing, was −39.58 ± 0.89 cal mole^{-1} PbO.[252] Concentrated sulphuric acid has been used as solvent.[253] The authors cited measured the enthalpies of solution of copper and cadmium selenochromites and Cu(Cd) + Cr + Se mixtures at 475 K, and calculated the enthalpies of formation of the selenochromites, which have the spinel structure. The results, together with the data for other transition metal sulphides and selenides,[253] were used to study the energies of formation in oxide–sulphide–selenide series and to examine the characteristic features of the formation of chalcogenide spinels. The results of the measurements of the enthalpies of solution of the oxides are given in Tables 5 and 6, and the enthalpies of the chemical compounds in Tables 7–10.

Table 10. Enthalpies of solution of chlorides in a high-temperature solvent (ΔH^0_T, kcal mole^{-1}).

M	MCl_2	$CsMCl_3$	Cs_2MCl_4	Cs_3MCl_5
Mn	2.75±0.04	14.08±0.04	12.24±0.08	14.31±0.10
Fe	3.63±0.04	14.88±0.06	14.11±0.11	15.90±0.13
Co	2.44±0.20	13.47±0.13	16.51±0.14	17.77±0.15
Ni	9.48±0.01	20.32±0.18	—	15.01±0.22
Cu	1.23±0.30	11.25±0.30	11.55±0.25	14.05±0.32
Zn	−3.75±0.30	—	15.90±0.21	16.60±0.10
Zn	−6.20±0.30[b]	—	—	—
Ca	1.04±0.13	12.52±0.03	—	—
Cs[a]	1.46±0.02	—	—	—

Notes: [a] CsCl; [b] $ZnCl_2$(liquid).

Data on calcium, magnesium, and lead silicates have been used in a comparison of the results of the determination of the enthalpies of formation of silicates from the oxides by classical calorimetry involving solution in aqueous acid solutions (hydrofluoric acid) and high-temperature microcalorimetry involving solution in solvent melts (Table 11).

¶ The enthalpies of solution of $Fe_{1-x}O$ (where x = 0.0485 to 0.1166) in the same melt at 1179 K have been measured.[405]

Table 11. Comparison of the enthalpies of formation of silicates from the oxides (kcal mole^{-1}), determined by high-temperature solution microcalorimetry in molten $2PbO.B_2O_3$ (I) and solution calorimetry in aqueous HF (II) at 298 K.

Compound	Method I	Method II
$CaSiO_3$	−21.01±0.25 [137]	−21.25±0.11 [125]
$MgSiO_3$	−7.61±0.27 [17]	−8.69±0.15 [125]
Mg_2SiO_4	−13.90±0.33 [17]	−15.12±0.21 [125]
Mg_2SiO_4	—	−13.86±0.30 [135]
$CaMgSi_2O_6$	−34.99±0.41 [137]	
$CaMgSi_2O_6$	−33.35±0.47 [184, 185]	−35.25±0.22 [135]
$PbSiO_3$	−4.3±0.3 [223]	−4.2±0.5 [134]

Note. Numbers in square brackets denote references (Ed. of Translation).

4. Phase Transformations

High-temperature solution microcalorimetry can be used to study the enthalpies of phase transformations by successively dissolving the two phases of the same chemical compound (mineral) under identical conditions (temperature, solvent composition, solute concentration). The enthalpy of a phase transformation is generally small (often <0.5 kcal mole^{-1}), and since it is determined from the difference between the large values of the enthalpies of solution of the two phases, the uncertainty is high,[86,196,254] and amounts to ~0.2 kcal mole^{-1}. Much better results can be obtained by the direct determination of the enthalpy of the transformation by simultaneously dissolving the two phases in the two cells of a differential HTMC.[229,255] These methods have been used to study the enthalpies of polymorphic transformations, phase transformations, and fusion, the enthalpies of formation of solid solutions, and the enthalpies of processes involving the disordering of solid phases, by dissolving the appropriate specimens in melts with the compositions $3Na_2O.4MoO_3$,[256,257,229] $2PbO.B_2O_3$,[181,196,205,254,258–265] $9PbO.3CdO.4B_2O_3$,[86,104,164,266] and $LiBO_2$–$NaBO_2$ [220] (Table 12).

Table 12. Enthalpies of phase transformations, determined by dissolving the phases in a melt (ΔH^0_T, kcal mole^{-1}).

Compound	Transformation	T, K	ΔH^0_T	Refs.
Al_2O_3	$\alpha \rightarrow \gamma$	978	−5.3	164
Al_2O_3	$\varkappa \rightarrow \alpha$	978	3.6	164
Al_2O_3	$\delta \rightarrow \alpha$	978	−2	164
SiO_2	quartz → coesite	970	0.7±0.1	86
SiO_2	quartz → stishovite	970	1.4±0.1	86
SiO_2	quartz → cristobalite	970	0.45±0.15	86
SiO_2	cristobalite → liquid	966	2.5±0.2	86
Ni_2SiO_4	olivine → spinel	986	1.4±0.7	254
$CaSiO_3$	$\beta \rightarrow \alpha$	971	1.26±0.31	196
$MnSiO_3$	rhodonite → pyroxyoptite		0.1±0.3	265
$CaMgSi_2O_6$	diopside → glass	986	21.0±0.3	265
Al_2SiO_5	andalusite → sillimanite	973	0.67±0.23	168
$Mg_2Al_4Si_5O_{18}$	cordierite-K → cordierite glass	963	54±2	181
TiO_2	brookite → rutile	971	−0.17±0.09	256
TiO_2	anatase → rutile	971	−0.78±0.20	256
TiO_2	anatase → rutile	968	−1.57±0.15	225
$CdTiO_3$	$\alpha \rightarrow \beta$	965	3.58±0.18	257
GeO_2^*	tetragonal → hexagonal	965	5.18±0.25	408
GeO_2^*	hexagonal → vitreous	965	3.7±0.6	408

*Phase transformations: tetragonal structure → hexagonal structure, hexagonal structure → vitreous phase.

IV. THERMOCHEMICAL STUDY OF GAS–SOLID REACTIONS

High-temperature microcalorimetry can be used to measure the enthalpies of heterogeneous solid + gas chemical reactions. Procedures for measuring the enthalpies of oxidation were examined in detail in a study of the oxidation of niobium.[267] The influence of the oxygen pressure and the temperature of the experiment on the form of the heat-liberation curve was studied, and the thermal effects of the successive stages of the oxidation: the dissociation and adsorption of oxygen, diffusion, and the formation of compounds on the surface, were examined. The results of this study were used to develop a method for the microcalorimetric study of heterogeneous reactions of solids with gases to give new solid compounds.

The calorimeter for the study of M + O_2 systems is calibrated from the known enthalpy of oxidation to give an oxide with a definite composition, or from the enthalpy of another chemical reaction.[268] Since the calibration constant may change from one experiment to another (for example, $K_1 = 100$, $K_2 = 120$, $K_3 = 130$), but remains constant during a given experiment, the HTMC are calibrated immediately before the experiment or immediately after it.[93] The enthalpy of the oxidation of thorium to ThO_2 has been recommended[93] for calibration. In the study of M + H_2 systems, the calibration is carried out either electrically or by mixing, since the partial enthalpies of solution of hydrogen are ~10 kcal, and in this case the quantity $0.5RT \cong 0.7$ kcal mole^{-1} cannot be neglected; it can be neglected, however, for the enthalpies of solution of oxygen (oxidation), amounting to ~80 kcal[268] ($0.5RT \cong 1.3$ kcal mole^{-1}).

The procedure involving the study of gas + solid reactions was used to measure the enthalpies of the oxidation of metals by oxygen.[95] Kleppa and co-workers[269–272] measured the enthalpies of the oxidation of tungsten, vanadium, niobium, and tantalum and the lower oxides of tungsten, vanadium, and titanium to give WO_3, V_2O_5, NbO_x, and TiO_2 respectively at temperatures of ~1100 K, and the heat of solution of O_2 in the non-stoichiometric phase TiO_x at 1323 K has been measured.[273] A similar procedure was used[274,275] to measure the enthalpies of oxidation of the lower oxides of praseodymium and terbium at 713 K and of the lower oxides of cerium ($CeO_{1.5}$–$CeO_{1.95}$) at 1353 K,[94] plutonium ($PuO_{1.5}$–$PuO_{1.71}$), and uranium[277,276,97] to give CeO_2, $PuO_{1.61}$, PuO_2, and U_3O_8 respectively. The enthalpies of oxidation of cerium oxides[94] have been compared with the results obtained by studying the equilibrium $CeO_{1.5}$ + $O_2 \rightleftharpoons CeO_2$; the difference in the enthalpies of oxidation for the composition $CeO_{1.86}$ is less than 3 kcal. The uncertainty of the measurements of the enthalpies of oxidation of plutonium oxides[278] was 2%. The enthalpies of oxidation of non-stoichiometric iron oxides (FeO_{1+x}) were studied at 1073 K for $x = 1.05$–1.109 and at 1348 K for $x = 1.040$–1.140.[96,98,279] The partial enthalpies of solution of oxygen were measured; for the compositions FeO_{1+x} ($x = 0.040$–0.140), the enthalpies of mixing were 120.2–133.6 kcal mole^{-1}, and the values given for ΔH^0_{0x} increase linearly with increase in Δx.

The enthalpy of the chemisorption of oxygen on zinc powder has been determined[280] at 303.7 K and 451.1 K. The values obtained from the results of 15 experiments at 303.7 K (165–170 kcal mole^{-1} O_2) and at 451.1 K (166.0–176 kcal mole^{-1} O_2) are close to the standard enthalpy of formation of ZnO ($\Delta H^0_{f\,298} = -167.6$ kcal mole^{-1} O_2). The results confirm that it is possible in principle to use high-temperature microcalorimetry to study gas–solid reactions, and also that the method is suitable for the study of sorption processes and the reactions involved in the formation of non-stoichiometric compounds.

The adequate reliability of the measurements of the enthalpies of oxidation of "comparatively simple materials" (metals and oxides) enabled a number of authors to use the same procedure to study the oxidation of more complex oxygen compounds. Thus the enthalpy of oxidation of titanium oxide nitride at 1500 K according to the scheme:

$$TiO_xN_y + 0.5\,x\,O_2 \rightarrow TiO_2 + 0.5\,y\,N_2$$

has been determined.[281] Since the procedure is fairly complicated, the uncertainty of the experiment was estimated as 5%, which is greater than that of other microcalorimetric procedures, for example that involving the measurement of enthalpies of solution. The enthalpy of oxidation of cerium orthoferrite by atmospheric oxygen according to the equation:

$$CeFeO_3 + 0.25\,O_2 \rightarrow CeO_2 + 0.5\,Fe_2O_3$$

was measured at 975 K [282] by dropping the specimens, brought to constant temperature at 298 K, into the calorimeter cell. A similar procedure was used[258,283] to determine the enthalpies of oxidation of double sulphides of cobalt, iron, molybdenum, gallium, and copper. The enthalpies of the reactions of the type:

$$CoCr_2S_4 + 7\,O_2 \rightarrow CoCr_2O_4 + 2\,SO_2 + 2\,SO_3 \quad (975\ K)$$
$$Ga_{2/3}Mo_2S_4 + 9.5\,O_2 \rightarrow 1/3\,Ga_2O_3 + 2\,MoO_3 + 4\,SO_3 \quad (920\ K)$$

are given in Table 13. Non-stoichiometric iron sulphides have been studied by oxidising Fe.[284] The following reaction took place in the calorimeter cell at 555 K:

$$(1-0.4\,x)\,FeS + 0.4\,x\,O_2 \rightarrow Fe_{1-x}S + 0.2\,x\,Fe_3O_4$$

with enthalpy $\Delta H^0_{555} = -(23.1 \pm 1.4)x$, and the enthalpy of formation of the sulphides is:

$$\Delta H^0_{f555}\,(Fe_{1-x}S) = \Delta H^0_{f555}\,(FeS) + (10.0 \pm 1.8)\,x,\ x = 0 - 0.125$$

The results of the study of solid + oxygen reactions indicate the extensive possibilities provided by the procedure being considered for the thermochemical study of heterogeneous solid + gas chemical reactions. This is confirmed by studies of the high-temperature thermochemistry of M + H_2 systems, which from the calorimetric viewpoint are analogous to the reactions involved in the oxidation of metals. The solution of hydrogen and deuterium in metals, alloys, or solid solutions of M–H_2 or M–D_2 systems has been studied. The partial enthalpies have been measured[285,286] for the solution of hydrogen in lanthanum, yttrium, and their hydride phases at 917 K and 919 K, in vanadium, niobium, and tantalum and their solid solutions with hydrogen at 264, 300, and 437 K (V), 356 K and 440 K (Nb), and 700 K and 703 K (Ta), and in thorium at 700 K.[287–289] The thermodynamic properties of solutions of H_2 and D_2 in palladium at 770–970 K, in manganese at 550–700 K, and in the alloys Pd–Au (10.25% and 40% Au) and Pd–Cu (10.25% and 40% Cu) at 555 K and 700 K, and Pd–Ag and Pd_3Mn at 555–909 K have been measured.[290–297]

The temperature dependence of the enthalpy of solution of hydrogen has been measured in dilute PdH_x solutions at 555–712 K [238] and in Pd at 518–625 K and pressures up to 34 atm. The reaction of H_2 and D_2 with α-Zr has been studied,[299,300] and the enthalpies of solution determined. The solution of hydrogen in $LaNi_5$–$CaNi_5$ alloys at 298 K has been studied.[287]

Most studies showed that the enthalpies of solution are practically independent of the temperature at which the measurements are made. In a series of remarkable studies,[287,290–293] the microcalorimetric procedure was combined with a flow method for studying heterogeneous equilibria (gas–solid) to determine both ΔH^0 and ΔG^0 for the formation of hydride

phases. In these studies, as in other work,[288,289] good agreement was observed between the results of the measurements by two independent methods. The combination of the results of the microcalorimetric experiment (the enthalpy of the solid + gas reaction) with the results of the study of the equilibria in the same system (the Gibbs function) makes it possible to determine more accurately the fundamental thermodynamic functions of the solid–gas system and to use them to model the geological processes involved in the reaction of minerals with hot gas mixtures (H_2, O_2, N_2), in the study of sulphide equilibria and the solid phases in meteorites,[139,140] and to construct gas–metal equilibrium diagrams in metallurgy.[93–98] Table 14 compares the enthalpies of oxidation determined by high-temperature microcalorimetry with data obtained by combustion calorimetry in an oxygen bomb.

Table 13. Enthalpies of oxidation ($-\Delta H^0_T$, kcal mole^{-1}).

Starting material	Oxidation products	T, K	$-\Delta H^0_T$	Refs.
Zn	ZnO	303.7	(165÷170)	[280]
Zn	ZnO	451.1		
W	WO_3	910	198.94	[269]
WO_2	WO_3	910	60.52±0.65	[269]
$WO_{2.72}$	WO_3	910	14.84±0.16	[269]
$WO_{2.96}$	WO_3	910	6.30±0.06	[269]
$CeO^a_{1.5}$	$CeO_{1.65}$	1353	178	[94]
$CeO^a_{1.72}$	$CeO_{1.85}$	1353	198	[94]
$CeO^a_{1.85}$	$CeO_{2.00}$	1353	222	[94]
Pr_7O_{12}	PrO_{2-x}	713	58	[274]
$TbO_{1.5+x}$	Tb_7O_{12}	713	54	[275]
$TiO_{0.81}$	TiO_2	1100	119.72±1.05	[271]
$TiO_{0.89}$	TiO_2	1100	108.24±1.35	[271]
TiO	TiO_2	1100	95.82±1.09	[271]
$TiO_{1.05}$	TiO_2	1100	89.97±1.03	[271]
$TiO_{1.17}$	TiO_2	1100	82.43±1.06	[271]
$TiO_{1.20}$	TiO_2	1100	75.75±0.63	[271]
$TiO_{1.26}$	TiO_2	1100	71.34±1.03	[271]
$TiO_{1.5}$	TiO_2	1100	45.42±0.60	[271]
$TiO_{1.67}$	TiO_2	1100	31.19±0.43	[271]
$FeO_{1.05-1.15}$	$FeO_{1.5-x}$	1348	120–134	[98]
$VO_{1.5}$	V_2O_5	910	39.35±0.42	[270]
$VO_{5/3}$	V_2O_5	910	27.26±0.31	[270]
$VO_{7/4}$	V_2O_5	910	24.16±0.40	[270]
$VO_{9/5}$	V_2O_5	910	22.75±0.30	[270]
$VO_{11/6}$	V_2O_5	910	21.71±0.23	[270]
$VO_{15/8}$	V_2O_5	910	21.0±0.30	[270]
VO_2	V_2O_5	910	14.97±0.34	[270]
$VO_{13/6}$	V_2O_5	910	8.94±0.1	[270]
$FeS + SO_2$	$Fe_{1-x}S + Fe_3O_4$	555	(23.1±1.4)x	[284]
TiO_xN_y[b]	$TiO_2 + N_2$	1500	(116.4–68.0)	[281]
$CeFeO_3$	$CeO_2 + Fe_2O_3$	975	26.10±0.30 (298 K)	[282]
UO_2	$UO_{2.242}$	1323	8.75	[410]
$Ga_{2/3}Mo_2S_4$	$Ga_2O_3 + MoO_3^+SO_3$	920	703.8±1	[283]
$PuO^a_{1.5}$	PuO_2	1373	210±5	[278]
$PuO^a_{1.61}$	PuO_2	1373	214±5	[278]
$PuO^a_{1.5}$	$PuO_{1.61}$	1373	197	[278]
$PuO^a_{1.61}$	$PuO_{1.70}$	1373	195	[278]
$PuO^a_{1.70}$	$PuO_{1.71}$	1373	175	[278]
$PuO^a_{1.71}$	PuO_2	1373	221	[278]
$CoCr_2S_4$	$CoCr_2O_4 + SO_2 + SO_3$	975	548.5±1.2	[241]
$FeCr_2S_4$	$Fe_2O_3 + Cr_2O_3 + SO_2 + SO_3$	975	565.4±1.7	[241]
$CuCr_2S_4$	$CuO + Cr_2O_3 + SO_2 + SO_3$	975	516.4±1.6	[241]

Notes: [a] kcal mole^{-1} O_2; [b] x = 0.72–0.16; y = 0.3–0.47.

Table 14. Comparison of the enthalpies of formation of oxides ($-\Delta H^0_{f\,298}$, kcal mole^{-1}), determined by high-temperature microcalorimetry from the enthalpy of oxidation and by combustion calorimetry in an oxygen bomb.

Starting material	Oxidation product	HTMC		Calorimetry	
W	WO_3	198.94	[269]	201.4±0.2	[134]
WO_2	WO_3	140.19±0.70	[269]	140.9±0.2	[134]
$WO_{2.72}$	WO_3	186.34±0.27	[269]	185.4±2.0	[134]
$WO_{2.90}$	WO_3	195.08±0.22	[269]	195.6±2.0	[134]
Zn	ZnO	82.5–85.0	[280]	83.80±0.06	[134]
$PuO^a_{1.51}$	$PuO_{2.00}$	207±7	[278]	206±2	[278]
$PuO^a_{1.57}$	$PuO_{2.00}$	210±7	[278]	208±2	[278]

Notes: [a] enthalpies of oxidation in kcal mole^{-1}; [b] T = 450 K.

Note. Numbers in square brackets denote references (Ed. of Translation).

V. THE STUDY OF THE DISSOCIATION OF SOLIDS

Studies of the enthalpies of dissociation of solids are methodologically similar to microcalorimetric studies of solid + gas reactions. The dissociation, however, is accompanied by the liberation of the gaseous reaction product from the cell, with mass exchange between the contents of the cell and the surrounding medium and the removal of heat from the measurement zone. Thus in the study of dissociation it is important to take account of corrections for the removal of heat with the liberated gas. The use of an ampoule dropped into the calorimeter cell makes it possible to avoid mass transfer of gas and corresponding heat loss.

The largest number of studies using this procedure have been devoted to crystalline hydrates and metal carbonyls. The enthalpies of dehydration of the calcium aluminates $CaAl_2O_4.10H_2O$, $Ca_2Al_2O_5.8H_2O$, and $Ca_3Al_2O_6.6H_2O$,[303] and the dissociation of potassium hydrogen phosphates,[118] accompanied by the liberation of water:

$$K_2HPO_4 \rightarrow 0.5\,K_4P_2O_7 + 0.5\,H_2O\,(gas)$$
$$2\,K_2HPO_4 + KH_2PO_4 \rightarrow K_5P_3O_{10} + 2\,H_2O\,(gas)$$

have been studied. The enthalpies of the reactions are given in Table 15. The enthalpy of dissociation of lithium sulphate monohydrate at 328–348 K and p = 0.7–5 mmHg is 14.7 ± 0.7 kcal mole^{-1};[304] the dissociation of calcium iodate hexahydrate at 323 K and 423 K has been studied.[305]

The dissociation of transition metal carbonyls in a double HTMC at 514, 534, and 543 K in an argon atmosphere has been studied.[306–309] The measurements were made by dropping glass ampoules with and without the substance into the differential cell. The measurements made it possible to determine the enthalpies of dissociation of Mn, Mo, and Cr carbonyls, and also the enthalpies of the reactions of the carbonyls with iodine vapour (Table 13). The enthalpies of the reactions studied were used to calculate the M–CC bond energies, where M is a transition metal. Similar methods were used[310] to study the reduction and bromination of uranium(III) oxide to the tetrabromide. The enthalpy of dissociation of lithium orthotitanate

$$Li_4TiO_4 + CO_2 = Li_2CO_3 + Li_2TiO_3$$

has been used[311] to determine the enthalpy of formation of the orthotitanate. The value obtained at 860 K and p_{CO_2} = 1 atm was 104.1 ± 0.7 kJ mole^{-1}. The dissociation of the double caesium nickel chloride, which takes place in the

solid phase, has been studied at 718 K by mixing (by dropping an ampoule containing the original Cs_3NiCl_5 [312] and repeated measurements by mixing to determine the difference $H_T - H_{298}$). A noteworthy feature of the last two methods for measuring the enthalpies of solid-phase decomposition is that the absence of gas liberation eliminates the additional experimental errors.

Table 15. Enthalpies of dissociation and iodination, kcal mole^{-1}.

Starting materials	Reaction products	T, K	ΔH_T^0	Refs.
$CaAl_2O_4 \cdot 10H_2O$	$CaAl_2O_4 + 10H_2O$	368	−35.4	[303]
$Ca_3Al_2O_5 \cdot 8H_2O$	$Ca_3Al_2O_5 + 8H_2O$	373	−16.5	[303]
$Ca_3Al_2O_5 \cdot 6H_2O$	$Ca_3Al_2O_6 + 6H_2O$	587	−88	[303]
$Ca(IO_3)_2 \cdot 6H_2O$	$Ca(IO_3)_2H_2O + 5H_2O$	323	65.87	[305]
$Ca(IO_3)_2 \cdot H_2O$	$Ca(IO_3)_2 + H_2O$	423	11.78	[305]
K_2HPO_4	$K_4P_2O_7 + H_2O$	598—653	11.0	[118]
$KH_2PO_4 + 2K_2HPO_4$	$K_5P_3O_{10} + 2H_2O$	573—673	32.4	[118]
$Cr(CO)_6$	$Cr + 6CO$	514	74±3	[306]
$Mo(CO)_6$	$Mo + 6CO$	534	81±3	[306]
$Mn_2(CO)_{10} + 2I_2$	$2MnI_2 + 10CO$	514	4.78	[306]
$Mo(CO)_6$	$Mo + 6CO$	534	81.1	[307]
$Cr(CO)_6$	$Cr + 6CO$	514	73.64	[307]
$Cr(CO)_6 + I_2$	$CrI_2 + CrI_3 + 6CO$	514	33.4	[307]
$Mn(CO)_5Br$	$0.5Mn + 0.5MnBr_2 + 5CO$	514	48.4	[308]
$Mn(CO)_5Br + 0.5\,I_2$	$MnBrI + 5CO$	514	16.6[a]	[308]
$Mn(CO)_5Cl$	$0.5Mn + 0.5MnCl_2 + 5CO$	543	37.1[a]	[308]
$Mn(CO)_5Cl + 0.5\,I_2$	$MnClI + 5CO$	514	14.5[a]	[308]
$Li_4TiO_4 + CO_2$	$Li_2CO_3 + Li_2TiO_3$	860	104.1±0.7	[311]
Cs_3NiCl_5	$CsNiCl_3 + 2CsCl$	718	7.3±0.1[a]	[312]
$Fe_2(CO)_9$	$2Fe + 9CO$	553—573	120	[309]
$Fe_2(CO)_9 + I_2$	$Fe + FeI_2 + 9CO$	524—573	118	[309]
$Fe_3(CO)_{12}$	$3Fe + 12CO$	494—544	123[a]	[309]
$Fe_3(CO)_2 + I_2$	$2Fe + FeI_2 + 12CO$	494—544	126[a]	[309]
$Co_2(CO)_8$	$2Co + 8CO$	470—475	98	[309]
$Co_4(CO)_{12}$	$4Co + 12CO$	514	124[a]	[309]
$Co_4(CO)_{12} + I_2$	$3Co + CoI_2 + 12CO$	456—518	124±4[a]	[309]
$Ru_3(CO)_{12}$	$3Ru + 12CO$	553—573	142[a]	[309]
$Rh_4(CO)_{12}$	$4Rh + 12CO$	518—574	119±3[a]	[309]
$Rh_6(CO)_{16}$	$6Rh + 16CO$	458—574	62±3[a]	[309]
$Re_2(CO)_{10}$	$2Re + 10CO$	593	129[a]	[309]
$Re(CO)_{10} + I_2$	$Re + ReI_2 + 10CO$	558—593	132[a]	[309]
$Os_3(CO)_{12}$	$30S + 12CO$	593	101[a]	[309]
$Ir_4(CO)_{12}$	$4Ir + 12CO$	594	118±4[a]	[309]
$UO_3 + 3C + 2Br_2$	$UBr_4 + 3CO$	775—878	9.1±0.2	[310]

Note: [a] T = 298 K.

VI. ENTHALPIES OF SYNTHESIS

A procedure analogous to that involving mixing in an HTMC can be used to study the enthalpies of formation of compounds during their preparation, for example during solid-phase synthesis. This method has not been widely used up to the present, however. In a study of the syntheses, the reaction of skinnerite with sulphur at 720 K to give the non-stoichiometric sulphides[313]

$$CuSbS_3 + x\,S \rightarrow CuSbS_{3+x}$$

and of liquid sulphur with FeS_x at 433 K [314] were studied. The results of the measurements [314] were used to determine the concentration dependence of the enthalpy of formation of iron sulphides, $\Delta H_{433}^0 = -22.2 \pm 11.8x$ kcal mole^{-1} for $0 \leq x \leq 0.095$ and also for $0 \leq x \leq 0.125$.

The enthalpies of formation of the double sulphides and selenides of gallium and thallium have been studied.[315] Stoichiometric mixtures of the sulphides (selenides), placed in an ampoule in the cell of an HTMC, were heated to 550—553 K for the sulphides and to 625 K for the selenides, and the enthalpy of the solid-phase synthesis on heating was determined:

$$Ga_2S_3 + Tl_2S_3 \rightarrow 2\,TlGaS_2,\ Ga_2Se_3 + Tl_2Se_3 \rightarrow 2\,TlGaSe_2$$

A similar procedure has been used to study the thermochemistry of the solid-phase reactions involved in the formation of manganese and boron carbides at 1320 K.[316,317]

VII. THERMOCHEMISTRY OF THE MIXING OF MOLTEN SALTS

The experimental study of the thermochemistry of molten salts was begun by Kleppa[38] with measurements of the enthalpies of mixing of melts of sodium and potassium nitrates at 619 K and 721 K. An ampoule containing a molten nitrate was placed in the cell of an HTMC containing the melt of the other nitrate (see Fig. 2*d*); the reaction began when the ampoule was broken using the manipulator. To increase the accuracy of the measurement, the effect of mixing was compensated by dropping specimens of gold, whose high-temperature enthalpy is known. This method was used to study the concentration dependence of the enthalpies of mixing in binary melts formed by the alkali metal nitrates[318] and in the mixtures $AgNO_3$–M^1NO_3,[319] M^1NO_3–$M^2(NO_3)_2$,[320—322] and $TlNO_3$–M^1NO_3,[323] where M^1 represents an alkali metal, and M^2 an alkaline earth metal. The enthalpies of mixing were also measured in the ternary systems formed by alkali metal nitrates with silver nitrate at $T < 723$ K.[324]

In all the systems studied, the values of the enthalpies of mixing increase regularly with increase in the differences in the sizes of the cations, but the sign of the effect shows no regularity. For most nitrate systems containing alkali metals, the enthalpies of mixing are negative. Some experimental data giving the dependence of the enthalpy of mixing on the mole fraction of a nitrate[38,318—324] are shown graphically in Fig. 7.

In spite of a theoretical treatment of the enthalpies of mixing, based on various assumptions,[325] and a review of experimental data,[318,319] regular features having "predictive power" could not be found. In accordance with the conformational theory of solutions, therefore, further studies of enthalpies of mixing were undertaken to examine the influence of the size and charge of the ions on the enthalpy of mixing.

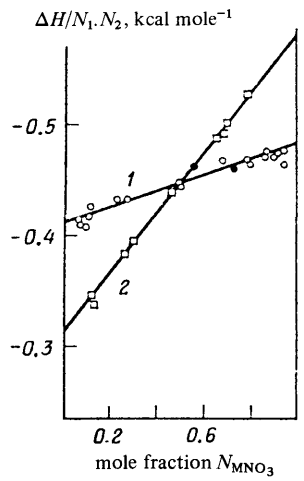


Figure 7. Dependence of the reduced enthalpy of reaction ($\Delta H/N_1.N_2$, kcal mole^{-1}) on the mole fraction of the nitrate (N_{MNO_3}) with the larger cation: *1*) KNO_3–$NaNO_3$, *2*) KNO_3–$AgNO_3$.

The enthalpies of mixing were studied for the halide systems MCl–M'Cl,[89–91,326,327] MCl–M'Cl–AgCl,[116,328] MCl–MCl_2,[329–333] MBr–MBr_2,[334] MCl_2–$M'Cl_2$,[335–338] and MI–M'I,[339] and the halide–nitrate systems MCl–MNO_3, MBr–MNO_3.[340–342] The use of halide melts, which are corrosive, made it necessary to modernise the HTMC to prevent the corrosive action of the halides. The inner metallic part of the calorimeter was protected by introducing a glass tube. Since the melting points of the halides are higher than those of the nitrates, the working temperature of the cell was increased to 1100 K,[320] or to ≥1300 K in the study of the fluorides.[343] The measurements were made in an atmosphere of nitrogen[319] or argon.[331] Before the experiment, the salts were placed in a quartz crucible and in a tube with an opening bottom (Fig. 8).

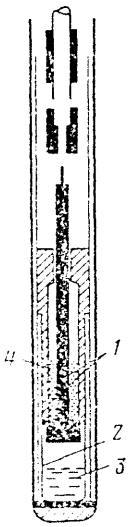


Figure 8. Reaction assembly for measuring the enthalpies of mixing of fluoride melts: *1*) ampoule with opening bottom, *2*) quartz cell, *3*) solvent (melt of the first component), *4*) melt of the second component.

For the study of molten alkali metal fluorides,[343,345] the inner parts of the HTMC were protected more thoroughly against corrosion.[343,344] The calorimeter cell containing the molten fluoride was made of platinum, and the melt of the second fluoride was placed in a platinum tube lowered into the first melt. The melts were mixed by displacing the melt from the tube by a graphite plunger (Fig. 9). This method was used to study the systems MF–M'F,[325,333] MF–MF_2,[344, 346–350] MF–AlF_3,[351,352] MF_2–MF_3,[351,352] MF–MCl, MF–MBr, and MF–MI.[353] The nature of the concentration dependence of the enthalpies of mixing of the fluorides differs from that for other halide systems (Fig. 10); there is considerable deviation from the linear relationship predicted by theory.[348] In the study of various chloride and more particularly fluoride systems, it was assumed that mixing leads to the formation of anionic complexes such as $PbCl_4^{2-}$, $PbCl_5^{3-}$,[329] MgF_4^{2-},[345] BeF_4^{2-}, and AlF_6^{3-}.[345,352]

The enthalpies of mixing have also been studied for oxygen-containing compounds such as carbonates,[354] sulphates,[355] metaphosphates,[160] and hydroxides,[357] and also WO_3(crystalline)–MWO_4(liquid),[358] Cs–CsCl,[359,360] LiF–Na_2SO_4, and Li_2SO_4–NaF.[361] A systematic analysis of experimental data was carried out by Kleppa,[22,342] and the data on binary salt melts was systematised.[363,364]

Thus high-temperature microcalorimetry has led to the accumulation of extensive experimental material with a high reliability. The influence of the size and charge of the ions (cation and anion) on the enthalpies of mixing of binary salt melts has been studied. Fig. 10 gives as an example the dependence of the reduced enthalpy of reaction $[\Delta H/N_1(1 - N_1)]$ on the mole fraction of the component with the smaller ion size.

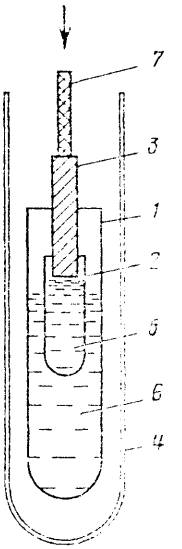


Figure 9. Reaction assembly for measuring the enthalpies of mixing of fluoride melts: *1*) platinum cell, *2*) platinum ampoule, *3*) graphite plunger, *4*) quartz cell, *5*, *6*) fluoride melts, *7*) plunger holder.

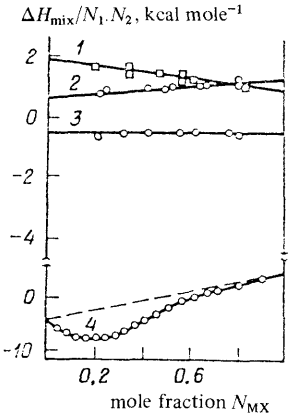


Figure 10. Dependence of the reduced enthalpy of reaction ($\Delta H/N_1.N_2$, kcal mole^{-1}) on the mole fraction (N_1) of the component with the smaller cation: *1*) LiCl–$PbCl_2$, *2*) LiBr–AgBr, *3*) $SrCl_2$–$BaCl_2$, *4*) LiF–BeF_2; N_1 is the mole fraction of the halide (MX) with the smaller cation, where X = chloride, bromide, or fluoride.

VIII. HIGH-TEMPERATURE ENTHALPIES AND ENTHALPIES OF PHASE TRANSFORMATIONS, DETERMINED BY MIXING

The high-temperature enthalpy of a chemical compound, mineral, or metal is determined by the classical thermochemical method of mixing calorimetry[365,366] by dropping a specimen with a mass of up to 20 g, heated in a furnace to the required temperature T, into a calorimeter cell at a constant standard temperature (298 K). The magnitude of the effect is determined by comparing with the values of the differences $H_T - H_{298}$ for standard substances (α-Al_2O_3, Pt, MgO, Au), used to calibrate the instrument.[135,367,368] This method is used to obtain the temperature dependence of $H_T - H_{298}$, and differentiation of this relationship with respect to T gives the temperature dependence of the mean heat capacity. When measurements are made by this method (hot → cold), sudden cooling (quenching) of the specimen is possible, and this may lead to the formation of metastable phases or structural defects and hence to errors which are eliminated only by additional measurments using other methods of study.

Cases of this kind were analysed in a study of the temperature dependence of the heat capacity of lithium ferrite,[348] where it was shown that the published values of $H_T - H_{298}$ for lithium ferrite, obtained by the classical method of mixing calorimetry, may contain a systematic error associated with the quenching of the specimen when it is dropped into the calorimeter cell.

In high temperature microcalorimetry, the specimen at the standard temperature of 298 K is dropped into the microcalorimeter cell heated to the required temperature T, after which the heat used to raise the temperature of the specimen is measured.[78,349] Thus in high-temperature microcalorimetry, the procedure (cold → hot) is the opposite of that in classical mixing calorimetry. High-temperature microcalorimetry makes it possible to eliminate the errors noted earlier. Another advantage of this method is the possibility of using specimens with a comparatively small mass (<1 g), thanks to the high sensitivity of the thermal detectors. The mass of the specimen is usually 100–300 mg.

Table 16. Coefficients of the Mayer–Kelley equation for lanthanide molybdates and ferrites[373,243,233,234,378,379] ($H_T - H_{298} = AT + BT^2 + CT^{-1} + D$).

Compound	A	$10^3 B$	$10^{-5} C$	D
$La_2(MoO_4)_3$	48.06	37.65	8.99	14 645
$Pr_2(MoO_4)_3$	87.14	15.93	25.27	35 846
$Nd_2(MoO_4)_3$	72.96	21.73	8.99	26 696
$Sm_2(MoO_4)_3$	66.91	23.64	−1.57	21 607
$Eu_2(MoO_4)_3$	74.89	22.60	9.00	27 386
$Gd_2(MoO_4)_3$	80.86	12.70	8.77	28 172
$Tb_2(MoO_4)_3$	71.00	18.55	1.87	23 340
$Dy_2(MoO_4)_3$	103.20	26.38	30.97	41 348
$Ho_2(MoO_4)_3$	81.60	12.99	9.00	28 543
$Er_2(MoO_4)_3$	52.02	32.21	−7.00	160 020
$Yb_2(MoO_4)_3$	83.55	97.70	8.99	28 821
$Lu_2(MoO_4)_3$	56.85	28.14	−3.00	18 367
$Y_2(MoO_4)_3$	85.34	53.06	9.00	28 949
$Sc_2(MoO_4)_3$	83.14	79.79	8.58	28 416
$LaFeO_3$	23.18	5.96	0.65	7 655
$PrFeO_3$	19.05	10.42	0.39	6 733
$NdFeO_3$	18.95	9.85	−0.74	6 275
$SmFeO_3$*	18.60	10.84	−0.53	6 328
$EuFeO_3$*	17.84	10.54	−2.37	5 457
$YFeO_3$	20.39	7.57	−1.29	6 316
$LuFeO_3$	22.45	5.47	−1.45	6 689
$Eu_3Fe_5O_{12}$**	32.56	61.32	−32.71	6 258
$Eu_3Fe_5O_{12}$**	129.3	0	0	42 930
$NaLa(MoO_4)_2$	41.21	51.63	7.008	10 260
$NaPr(MoO_4)_2$	269.39	24.76	0.5526	7 454
$NaNd(MoO_4)_2$	−7.643	−25.40	0.3137	—
$NaSm(MoO_4)_2$	−1.220	23.18	0.2928	2 680
$NaEu(MoO_4)_2$	58.58	54.88	0.6239	16 810
$NaGd(MoO_4)_2$	17.03	7.876	0.4517	5 993
$NaDy(MoO_4)_2$	40.40	48.27	0.6615	10 060
$NaHo(MoO_4)_2$	42.20	48.88	0.6541	10 530
$NaEr(MoO_4)_2$	42.62	41.02	0.5975	12 000
$NaYb(MoO_4)_2$	76.74	10.61	0.9620	17 480
$NaLu(MoO_4)_2$	40.42	39.63	0.6009	11 190
$NaY(MoO_4)_2$	69.41	85.99	0.8096	16 390
$NaSc(MoO_4)_2$	4.403	−18.26	0.3068	3 990
$Na_5La(MoO_4)_4$	−1.221	−23.18	0.2923	2 681
$Na_2Mo_2O_7$	89.89	129.48	1.0756	19 596
$Na_2Mo_4O_{13}$	−354.2	−72.20	−39.16	−55 000

*Temperature range 298–915 K. **298–573 K in the first row, 573–975 K in the second row, other compounds 298–973 K.

Table 17. Coefficients of the Mayer–Kelley equation for the high-temperature enthalpies of chemical compounds and minerals, and their heat capacities (C_p, cal mole^{-1} K^{-1}).

Compound	Coefficients of the Mayer–Kelley equation					T, K	Refs.
	A	B	C	D	C_p		
$Ca_3Al_2(SiO_4)_3$ (grossular)	92.02	16.03	17.29	34 658	82	298–1000	[382]
$Ca_3Fe_2(SiO_4)_3$ (andradite)	97.42	12.51	18.73	3 643	86	298–1100	[382]
$Mg_3Al_2(SiO_4)_3$ (pyrope)	87.51	16.38	18.63	33 796	76	298–1100	[382]
$KAl_3Si_3O_{10}(OH)_2$ (muscovite)	101.0	11.6	30.83	41 484	73.2	298–900	[384]
$KMg_3AlSi_3O_{10}(OH)_2$ (phlogopite)	106.03	13.39	24.75	41 103	86.2	298–1100	[384]
$K(MgFe_2)AlSi_3O_{10}(OHF)$ (biotite)	120.35	7.79	33.34	47 422	85.3	298–700	[384]
$Ca_2FeAlSi_3O_{12}(OH)$ (epidote)	113.78	7.35	28.92	44 276	85.6	298–1100	[385]
$Ca_2Fe_{0.3}Al_{2.7}Si_3O_{12}(OH)$ (clinozoisite)	120.18	3.86	33.01	47 248	85.3	298–1100	[385]
$Ca_2Al_2Si_3O_{12}(OH)$ (zoisite)	118.9	4.4	31.5	4 606	86.1	298–1100	[385, 384]
$Mg_7Al_{18}Si_3O_{40}$ (sapphirine)	184.75	9.46	55.4	74 509	128.4	298–1000	[188]
$CaBSiO_4(OH)$ (datolite)	−90.12	26.8	11.15	—	33.66	298–973	[386]
$CaB_2Si_2O_8$ (danburite)	12.26	34.22	22.88	—	—	298–973	[386]
β-BN	7.67	1.74	4.73	4030	—	298–1100	[389]
$NaBeF_3$(liquid)	43 100	160.8	—	—	—	298–1025	[349]
$NaBeF_3$(crystalline)	13 900	9.3	—	—	—	298–1025	[349]
β-Na_2BeF_4(crystalline)	84 100	237.3	—	—	—	448–593	[349]
α-Na_2BeF_4(crystalline)	46 200	155.0	—	—	—	298–448	[349]
γ-Na_2BeF_4(crystalline)	52 300	191.8	—	—	—	593–863	[349]
Na_2BeF_4	83 900	255.8	—	—	—	863–1025	[349]

Table 18. High-temperature enthalpies and enthalpies of phase transformations (kcal mole^{-1}).

Compound	$H_T - H_{298}$; ΔH^0_T	T, K	Refs.
SiO_2 (quartz)	10.46	298–968	[86]
SiO_2 (coesite)	11.65	298–1072	[86]
α-PbO_2	6.233	298–657	[86]
α-PbO_2	6.454	298–599	[86]
TiO_2 (rutile)	10.953	294–965	[390]
GeO_2	10.624±0.015	295–966	[408]
$Li_2Ti_3O_7$	49.87	300–1000	[390]
$Li_{4/3}Ti_{5/3}O_4$	26.97	300–1000	[390]
$La_{0.95}Ca_{0.05}CrO_3$	19,92±0.19	346–938	[376]
$Y_{0.85}Ca_{0.15}CrO_3$	14,72±0.15	382–885	[376]
$CuCr_2S_4$	29.2±0.5	298–975	[380]
$FeCr_2S_4$	29.1±0.5	298–975	[380]
$CoCr_2S_4$	28.7±0.5	298–975	[380]
$NaVO_3$	24,53	298–923	[403]
$CaMgB_2O_5$	30.4±0.4	298–973	[401]
$LiNO_3$ (crystalline-liquid)	5.961±0.083	527	[402]
$NaNO_3$(crystalline-liquid)	3.696±0.032	583	[402]
KNO_3 (crystalline-liquid)	2.413±0.028	610	[402]
$PbNO_3$(crystalline-liquid)	1.105±0.010	589	[402]
$CsNO_3$ (crystalline-liquid)	3.213±0.043	690	[402]
$AgNO_3$(crystalline-liquid)	2.886±0.008	483	[402]
$TlNO_3$(crystalline-liquid)	2.264±0.036	479.5	[402]
$CoTiO_3$*	−1.66±1.02	298	[391]

*Defect spinel–ilmenite phase transformation.

The mixing method using HTMC began to be widely used after the publication of the first studies[86,370] and the development of an automatic device for dropping the specimens.[87] The accuracy of the results obtained by this method is higher when a compact specimen (crystal or tablet) is used. Powdered specimens are placed in a special ampoule made of Pt or Ag, and the heat capacity of the ampoule should not be greater than 15% of the total heat capacity of the specimen and the ampoule.

The improvement of the experimental procedure has made it possible to carry out measurements with extremely small specimen masses (2–10 mg) in the range 400–1100 K;[371,372] the use of a special device (see Fig. 1*b*) led to a marked increase in the sensitivity of the measurements. The heat-absorption time was decreased by a factor of 2, from 70 s to 25–30 s. When the temperature of the HTMC block is kept constant to within ±0.1 K, the uncertainty of the measurements is 2%.

As a consequence of these advantages, the method involving mixing using HTMC has been widely used, for example to determine the temperature dependence of the enthalpy and heat capacity of simple and double molybdates of the lanthanides and yttrium,[243–245,373–375] yttrium and lanthanum chromites,[376,377] yttrium and lathanide ferrites,[233,378,379] double sulphides of chromium, iron, cobalt, and copper,[283,380] quartz,[86] borosilicate and aluminosilicate minerals,[381,386] and a number of other substances and minerals.[40,162,349,387–392] The results of the experimental measurements, treated using the Mayer–Kelley equation and also using a special programme,[393] are given in Tables 16–18.

The method of mixing using HTMC also make it possible to study the energies of the transformations taking place when the dropped specimen is heated. Thus the enthalpy of the volatilisation of MoO_3 was measured by dropping MoO_3 (298 K) into an HTMC cell heated to 1086.1 K and 1119.4 K [373] and weighing after keeping for different time intervals; a similar method was used to determine the enthalpy of fusion of $NaBeF_3$.[349] The method of mixing from 298 K to 1083 K [391] was used to study the enthalpy of the defect spinel–ilmenite transformation in a $CoTiO_3$ specimen, and the phase transformation in TiO_2.[396] Most studies, however, have been devoted to the sublimation, volatilisation, or fusion of metals, for example the study of the enthalpy of the sublimation of zinc and tellurium at 1093 K [397,398] and of cadmium at 590 K;[399] an extremely large amount of experimental data has been obtained, and it cannot be examined in the present review.

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While the present review was being prepared for publication, new papers appeared on the study of the theory[411] and practice[412,413,414] of high-temperature microcalorimetry, the thermochemical properties of lanthanide oxides, manganese borides, iron and aluminium vanadates, alkali metal perrhenates, lanthanide tungstates, and ferrite solid solutions,[415–420] and also on the thermochemistry of minerals.[421–423]

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