Translated from *Uspekhi Khimii*, 48, 2164-2174 (1979) U.D.C. 541.11

Thermochemical Studies Necessary for the Selection of Key Thermodynamic Quantities

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The present state of experimental studies necessary for calculating key thermodynamic quantities has been reviewed. A list of substances for which experimental measurements of the enthalpies of formation, entropies, etc. are desirable has been proposed. Various problems in the calculation of the standard thermodynamic quantities for solutions have been examined. A list of international recommendations on key thermodynamic quantities has been given. The bibliography contains 50 references.

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I. INTRODUCTION

Thermodynamic quantities such as the enthalpy and free energy of formation and entropy represent a system of inter-related quantities. Thus the enthalpy of formation of methane depends on the values of the enthalpy of formation of H_2O and CO_2. The free energy, enthalpy of formation, and entropy of a substance are related by the equation $\Delta G = \Delta H - T\Delta S$. Thus with the exception of the standard entropy, the choice of the numerical value of a thermodynamic quantity from published data, or its calculation from experimental measurements, usually cannot be made without certain calculations using various other quantities. The quantities which are most frequently used in these calculations are usually called key thermodynamic quantities.

The quantities usually regarded as key quantities are the values of the enthalpy of formation and entropy at 298.15 K and the enthalpy $H^0_{298} - H^0(0)$ for such substances (basic(as H_2O (liquid, gas), CO_2(gas(, HF (gas), SiO_2 (α-quartz), NH_3 (gas), NH_3 (gas), O_2 (gas), H (gas), B (gas), Cl^- (aq), SO_4^{2-} (aq), Na^+ (aq), UO_2^{2+} (aq), etc.; that is the basic substances are usually elements in their standard states and in the state of free atoms, and also one or two compounds of each element and ions in the state of a standard aqueous solution. This is because these substances appear most frequently in thermochemical cycles and other calculations; the choice of values for these quantities influences the numerical values of the thermodynamic properties of a large number of other substances. Thus the values of the enthalpies of formation of H_2O and CO_2 appear in the calculation of the enthalpies of formation of a vast number of organic compounds, and the values of the thermodynamic properties of simple aqueous ions in the ground state appear in the calculation of the thermodynamic characteristics of solutions of acids, alkalis, salts, undissociated ionic complexes, and many salts in the crystalline state.

The choice of key quantities obviously acquires particular importance in the preparation of fundamental reference books on the thermodynamic properties of substances, summarising accumulated experimental material. The most important principle in the production of these reference works — the internal consistency of the values given — requires recalculation of the results of all experimental studies using the same key quantities. Here it is necessary to take account of the fact that, as shown by the experience of the US National Bureau of Standards[1,2] and the Academy of Sciences of the USSR[3,4], the complete production and publication of these fundamental reference works require about 15 years. Simply as a consequence of the fact that the work on the production of these reference books was begun at different times, the values of the thermodynamic properties given in them are based on different key quantities. When these reference works are used, particularly in the calculation of precise experimental measurements, it is necessary to take account of these differences and to avoid the use of values which are inconsistent with one another.

All the inconvenience and the possibility of misunderstanding and confusion introduced by differences in the values of key quantities are obvious. In order to at least partly eliminate these unsatisfactory features immediately and to remove them completely in the future, the Committee On Data For Science And Technology (CODATA) of the International Council Of Scientific Unions in recent years has been preparing single international recommendations of key thermodynamic quantities. Values have already been chosen for 125 substances, and the preparation of recommendations for several more tens of substances is being completed; some of these quantities have been published[5,6]. A complete summary Table is given in the Appendix at the end of the present review.

One of the aims of the present work is to draw the attention of experimentalists to these international recommendations and to discuss various characteristic features of their use in the calculations. It is necessary that in the future these recommendations become a general basis for calculating the results of experimental measurements and in the production of reference works. It should be borne in mind that the reference books widely used as a source of supplementary thermodynamic quantities[1-4] are based on key quantities which do not coincide with new international recommendations. Thus when the latter are used, it is necessary to introduce appropriate corrections to the data from reference works, which is not always easy.

In view of the situation which has now arisen, where in the literature there is lack of agreement on the choice of key quantities, and reference works on the thermodynamic properties of substances are based on different key quantities (which moreover do not coincide with prepared international recommendations), it is appropriate, in the opinion of the present authors, to make the

following recommendations as practical advice to authors of experimental papers. In those cases where the key quantities recommended by CODATA are sufficient (or almost sufficient) for the recalculation, these should be used. In those cases where the necessary recalculations are complex, and a large number of quantities other than those recommended by CODATA are required, it is preferable to use any one of the above mentioned reference works, since this guarantees that the values included in the calculations are consistent with one another. In any case, it is necessary to indicate in published work the source of the supplementary data used in the calculations (as required by an international resolution on the publication of calorimetric and thermodynamic data[7]). The observation of this and other requirements of the resolution[7] ensures the validity of the publication and makes it possible to estimate the reliability of the measurements made and to recalculate the results using other key quantities.

It is to be hoped that the confused situation discussed above, which has arisen as a result of differences in the values of key thermodynamic quantities used in reference works and in individual publications, will be eliminated in the comparatively near future, since it is planned, about 1980, to begin the preparation of an international reference work on the thermodynamic properties of substances.

II. EXPERIMENTAL STUDIES OF PARTICULAR INTEREST FOR THE SELECTION OF KEY THERMODYNAMIC QUANTITIES

The chief aim of the present work is to attempt to draw the attention of experimentalists to various studies of particular interest from the viewpoint of the values of key thermodynamic quantities (and hence from the viewpoint of the production of the future international reference work). In course of work already rried out on the preparation of reference books and on the choice of key quantities, the available published data for a wide range of substances have been critically analysed. It has been found that the results of measurements for a number of the most important substances are insufficiently accurate or non-existent. At the same time, each year there are published the results of studies of a large number of less important substances, the selection of which is apparently determined by accidental factors. For example, in recent years an extensive cycle of studies on the determination of the thermodynamic properties of many tens of selenates has been carried out. However, the standard enthalpy of formation and entropy of the selenate anion, which are key quantities, have not yet been reliably determined, and the choice of these quantities is based on old and unreliable data. Unfortunately, this is not an isolated example. It would thus be extremely valuable if experimentalists, when planning their work, took account of the need for and importance of studies aimed at determining key thermodynamic quantities. These measurements should naturally be particularly careful and precise, and their publication sufficiently detailed.

Some of the most important experimental measurements which are particularly urgently required are listed below; for each type of measurement, the substances are arranged in order of importance and urgency.

1. Entropies of Crystalline Substances

Measurements of the low-temperature heat capacity and their use to determine the standard entropies and enthalpies of substances in the condensed state are particularly important, since standard entropies are usually determined more accurately than the enthalpies and free energies of formation†, and their use in the calculation of key quantities is almost always preferred to other possible methods. A list of substances for which determination of the standard entropies S^0_{298} is necessary is given below; the temperature ranges (in K) in which the heat capacities of these substances were measured are given in brackets: β-$Be(OH)_2$(crystalline); $MgCl_2$(crystalline) (51–298);[8] $CaCl_2$(crystalline) (51–298);[8] $PbCl_2$(crystalline) (15–206)[9]; PbF_2(crystalline); α-PbO(crystalline, red) (51–298);[10] Hg_2Cl_2(crystalline) (22–99)[11] and (100–273);[12] $HgCl_2$ (crystalline); HgO(crystalline, yellow); SnO_2(crystalline); SnO(crystalline) (69.6–292.5);[13] PuO_2(crystalline) (11–100)[14] and (4–25);[15] SeO_2(crystalline) (53.5–305);[16] α-TeO_2(crystalline); TeO_3(crystalline); α-Sb_2O_3(crystalline, cubic) (65–298);[17] β-Sb_2O_3(crystalline, orthorhombic) (56.2–298)[18] and (65–298);[17] Tl_2O(crystalline); Tl_2O_3 (crystalline); MnO(crystalline) (52–298);[20] Mn_2O_3 (crystalline) (50–298);[20] ReO_2(crystalline); ReO_3(crystalline) (2–100)[21] and (1.4–4.2);[22] Tc_2O_7(crystalline); PdO(crystalline); RuO_4(crystalline); RuO_2(crystalline) (0.54–10);[23] IrO2(crystalline) (0.54–10);[23] OsO_2(crystalline); α-WCl_6(crystalline); $MoCl_6$(crystalline); $Cd(OH)_2$ (crystalline); Ta_2O_5(crystalline) (53.4–294);[24] Au_2O_3 (crystalline).

2. Enthalpies of Formation

The measurement of the standard enthalpies of formation is required particularly urgently for the following substances in the condensed and gaseous states: SrO (crystalline), BaO(crystalline), $SrCl_2$(crystalline), $BaCl_2$ (crystalline), NO(gas), H_2S(gas), NH_4NO_3(crystalline), NH_4NO_2(crystalline), BeO(crystalline), α-$BeCl_2$(crystalline), $MgCl_2$(crystalline), $MgSO_4.6H_2O$(crystalline), AlI_3 (crystalline), $MgSO_4.7H_2O$(crystalline), SnO_2(crystalline), ThF_4(crystalline), $AlCl_3$(crystalline), $FeCl_2.4H_2O$(crystalline), $FeCl_3.6H_2O$(crystalline), TeO_2(crystalline), $TiCl_3$ (crystalline), Tl_2O(crystalline), Na_2WO_4(crystalline), Tl_2O_3(crystalline), V_2O_5(crystalline), $CrCl_3$(crystalline), $CrCl_3.6H_2O$(crystalline), $InCl_3$(crystalline), $GaCl_3$(crystalline), $MoCl_5$(Crystalline), $ScCl_3.6H_2O$(crystalline), $DyCl_3$ (crystalline), $LuCl_3$(crystalline).

For most of these substances, measurements of the enthalpy of the reaction with the corresponding metals present particular difficulties.

The direct measurement of the enthalpy of formation of ions in the standard state (that is in infinitely dilute aqueous solution) is impossible. This quantity is deter-

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†Here it should be borne in mind that the typical error of present-day measurements of the standard entropy (if there are no complicating features) is ~0.1 e.u. In the case of the calculation of the free energy or the equilibrium constant at 298 K, this error corresponds to an error in the enthalpy of the reaction of only 0.03 kcal $mole^{-1}$, which is not reached in all thermochemical measurements.

mined by extrapolating the results of measurements of the enthalpy of reaction, carried out at finite concentrations of the solution, to infinite dilution.

It should be noted that in most cases, including fundamental reference works[2,3], the standard heats of reactions in solutions at infinite dilution are determined by empirical extrapolation of the corresponding experimental data, obtained at definite ionic strengths of the solution I, to $I = 0$. These extrapolations have no rigorous theoretical basis; there are more rigorous methods of extrapolation, based on the electrostatic Debye–Hückel theory. As first shown in 1949,[25] in the determination of the form of the functional dependence of the enthalpies of dilution it is possible to use the equation for the mean-stoichiometric activity coefficients of the electrolytes $\gamma_\pm$ in the third approximation of the Debye–Hückel theory‡:

$$\lg \gamma_\pm = -\frac{|z_+ \cdot z_-| S_T \sqrt{I}}{1 + \mathring{B}a\sqrt{I}} + cI + bI^2 + \ldots, \quad (1)$$

where $S_T = 1.8246 \times 10^6\, d^{0.5}/(DT)^{1.5}$; $B = 50.294 \times 10^8\, d^{0.5}(DT)^{-0.5}$; d is the density of water; D the dielectric constant of water; T the temperature, K; z_i the charge of the ith ion; $I = \frac{1}{2}\Sigma m_i z_i^2$ is the ionic strength of the solution; $\mathring{a}$ the "ionic parameter"; and c and b empirical coefficients.

Using the familiar relationships

$$\bar{L}_2 = -\nu RT^2 \left(\frac{\partial \ln \gamma_\pm}{\partial T}\right)_{p,I}, \quad (2)$$

$$\bar{L}_2 = \varphi_H + m\frac{\partial \varphi_H}{\partial m} \quad (3)$$

and Eqn. (1), Owen and Brinkley[25] obtained in general form the dependence of the heat of dilution of electrolytes on the ionic strength of the solutions:

$$\varphi_H = \nu|z_+ \cdot z_-|\varphi_H\ (\text{D–H}) + c_H I + b_H I^2 + \ldots, \quad (4)$$

where $\nu|z_+ \cdot z_-|\varphi_H$(D–H) is the electrostatic contribution to the heat of dilution according to the Debye–Hückel theory, and c_H and b_H are empirical coefficients.

By solving Eqns. (1)–(3) simultaneously, Khodakovskii and Dorobeeva[26], independently of Owen and Brinkley, obtained an expression for φ_H(D–H):

$$\varphi_H\ (\text{D–H}) = \frac{S_H}{\mathring{B}a} J_1 + \frac{W_H}{(\mathring{B}a)^2} J_2, \quad (5)$$

where

$$J_1 = 1 - \frac{2}{\mathring{B}a\sqrt{I}} + \frac{2\ln(1 + \mathring{B}a\sqrt{I})}{(\mathring{B}a)^2 I}, \quad (6)$$

$$J_2 = 1 - \frac{4}{\mathring{B}a\sqrt{I}} + \frac{2}{(\mathring{B}a)^2 I}\left[\frac{1}{1 + \mathring{B}a\sqrt{I}} + 3\ln(1 + \mathring{B}a\sqrt{I}) - 1\right], \quad (7)$$

and the coefficients S_H and W_H are functions of only temperature and pressure, and their numerical values are given in Ref. 26. The same equations (5)–(7) can be obtained by substituting in the expression for φ_H(D–H) obtained in Ref. 25 the symbols used in Ref. 26, and carrying out the appropriate mathematical transformations.

‡ Only the basic scheme of the calculation is given below. More detailed descriptions can be found in Refs. 25 and 26.

It may therefore be assumed that the analytical form of the relationship (5) has been fairly reliably established.

Since the form of the equation for the dependence of the activity coefficients of individual ions on the ionic strength of the solution is similar to that of Eqn. (1):

$$\lg \gamma_i = -\frac{z_i^2 S_T \sqrt{I}}{1 + \mathring{B}a\sqrt{I}} + cI + bI^2 + \ldots, \quad (8)$$

it is possible, using the approach proposed by Vasil'ev[29], to obtain refined equations for calculating the standard enthalpy change (ΔH°) for any reaction involving ions:

$$\Delta H_I - \Delta z^2 \varphi_H\ (\text{D–H}) = \Delta H^0 + \Delta c_{H,I} + \Delta b_{H,I}^2 + \ldots, \quad (9)$$

where ΔH_I is the enthalpy change of the reaction for an ionic strength of the solution equal to I; Δz^2 the algebraic sum of squares of the charges of the ions taking part in the reaction (for example, for the reaction $CuCl_2 = Cu^{2+} + 2Cl^-$ we have $\Delta z^2 = 4 + 1 + 1 = 6$).

The applicability of Eqn. (9) in the determination of the standard heats of reactions from data for solutions having a high ionic strength (as far as $I = 3$–5) has been demonstrated[26–28]. The use of Eqn. (9) is particularly important in those cases where, from the conditions of the experiment, the calorimetric study of the reaction can be carried out only at high ionic strengths of the solutions, for example for reactions involving multiply-charged cations which are readily hydrolysed in weakly acidic solutions.

Table 1. Comparison of the standard enthalpies of various reactions, calculated using Vasil'ev's equation[29] and Eqn. (9).

Reaction	Δz^2	ΔH^0_{298}, kcal mole^{-1}		Refs.
		from Vasil'ev's Eqn.(29)	from Eqn.(9)	
$Co(cryst.) + H_2O_2(soln.) + 2H^+(soln.) = Co^{2+}(soln.) + 2H_2O(liq.)$	2	−104.07±0.15	−104.13±0.15	36
$Pb(cryst.) + H_2O_2(soln.) + 2H^+(soln.) = Pb^{2+}(soln.) + 2H_2O(liq.)$	2	−90.75±0.20	−90.80±0.20	30
$PbO(cryst., liq.) + 2H^+(soln.) = Pb^{2+}(soln.) + H_2O(liq.)$	2	−15.94±0.07	−15.98±0.07	30
$Fe(cryst.) + \frac{3}{2}H_2O_2(soln.) + 3H^+(soln.) = Fe^{3+}(soln.) + 3H_2O$	6	−147.25±0.15	−147.63±0.15	33
$SnCl_2(cryst.) = Sn^{2+}(soln.) + 2Cl^-(soln.)$	6	−3.22±0.30	−3.58±0.15	31
$SnCl_2.2H_2O(cryst.) = Sn^{2+}(soln.) + 2Cl^-(soln.) + 2H_2O(liq.)$	6	1.03±0.19	0.77±0.07	31
$Bi(cryst.) + \frac{3}{2}H_2O_2(soln.) + 3H^+(soln.) = Bi^{3+}(soln.) + 3H_2O(liq.)$	6	−117.7±1.2	−117.97±0.54	32
$Bi_2O_3(cryst.) + 3H^+(soln.) = Bi^{3+}(soln.) + \frac{3}{2}H_2O(liq.)$	6	−30.45±0.16	−29.86±0.15	32
$ZrCl_4(cryst.) = Zr^{4+}(soln.) + 4Cl^-(soln.)$	20	−70.64±0.29	−71.01±0.60	34
$ZrBr_4(cryst.) = Zr^{4+}(soln.) + 4Br^-(soln.)$	20	−73.39±0.15	−73.48±0.20	34
$HfCl_4(cryst.) = Hf^{4+}(soln.) + 4Cl^-(soln.)$	20	−80.14±0.31	−79.30±0.35	35

It should be noted that in spite of the fact that in the works cited[26,27], attention was drawn to the inaccuracy of the determination of the form of the functional dependence of φ_H(D–H) on the ionic strength of the solutions in Ref. 29, the equation derived in Ref. 29 is still often used (see for example Refs. 33–35) to calculate the standard enthalpies of reactions. Table 1 clearly shows that if the value of Δz^2 is large, the difference in the values of the standard heats of reactions obtained by different extrapolation methods may be considerable, and may exceed the error of the experimental measurements.

The most complex problem in the determination of the standard enthalpies of formation of simple ions which are key quantities is the measurement of the standard enthalpies of formation of such readily hydrolysed cations as Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Fe^{3+}, Cr^{3+}, Mn^{3+}, U^{4+}, Th^{4+}, Pu^{4+}, Sn^{4+}, Ge^{4+}, Zr^{4+}, Hf^{4+} and the anions SO_3^{2-}, $S_2O_3^{2-}$, SeO_3^{2-}, SeO_4^{2-}, TeO_3^{2-}, $Te(OH)_6^{2-}$, S^{2-}, Se^{2-}, Te^{2-}, etc. The standard enthalpies of formation of many of these ions can be determined by measuring the enthalpies of solution of the chlorides of the corresponding elements or their oxides in solutions of perchloric acid or alkali at concentrations of the latter which are sufficient for the practically complete suppression of hydrolysis. At the same time, quantitative allowance for the influence of hydrolysis processes also requires calorimetric measurements of the enthalpies of hydrolysis over a wide range of ionic strengths of the solutions.

3. Standard Entropies of Ions in Aqueous Solution

The most reliable values of the standard entropies for many simple cations and anions in aqueous solution in most cases are obtained from the value of ΔS°_{298} for the solution of the corresponding anhydrous salts or crystalline hydrates in water, in equilibrium with their saturated solutions:

$$K_m^{n+}A_n^{m-} \cdot xH_2O(\text{cryst.}) = mK^{n+}(\text{soln., standard state}) + nA^{m-}(\text{soln., standard state}) + xH_2O(\text{liq.}), \quad (10)$$

and also from the values of the standard entropy of the soluble salt, the entropy of the anion (or cation) and the entropy of H_2O(liquid) (in the case of crystalline hydrates). The values of ΔS°_{298} in turn is calculated from the values of ΔH°_{298} and ΔG°_{298} for reaction (10). For readily soluble salts, the reliable determination of the value of ΔG°_{298} is possible when there are experimental data on the mean-stoichiometric activity coefficients of the solutions $K_mA_n(\gamma\pm)$ and the activity of water in the case of crystal hydrates, up to the saturation concentration (m_{sat}). Since these calculations usually combine data obtained in different laboratories in methodologically different studies, generally not undertaken to solve the problem being considered in the calculations, the literature in many cases contains only some of the necessary data. Salts can be divided into three large groups, depending on the completeness of the available thermodynamic information.

The first group consists of salts for which it is sufficient to determine only one property in order to make possible the accurate calculation of the entropy of the cation (or anion). Thus for a number of salts there are reliable values of ΔS°_{298} for their solution (ΔG°_{298} and ΔH°_{298} for reaction (10) are known), but the calculation of the entropy of the ions cannot be carried out until sufficiently accurate values have been determined for the standard entropies of the corresponding crystalline substances. Accurate values of the latter can be obtained from measurements of the heat capacity in the temperature range 5–300 K. A list of these salts is given below; the temperature ranges (K) in which the heat capacities were measured are given in brackets.

β-$Be(OH)_2$, $MgSO_4\cdot 7H_2O$, $Mg(ClO_4)_2\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$ (295—305) [37], $CaCl_2\cdot 6H_2O$, $CaSO_4\cdot 2H_2O$ (50—298) [39], $Ca(ClO_4)_2\cdot 6H_2O$, α-$Ca(NO_3)_2\cdot 4H_2O$ (40—300) [38] and (295—305) [37], $SrCl_2\cdot 6H_2O$, $Sr(NO_3)_2\cdot 4H_2O$, $SrSO_4$ $SrCO_3$(50—298) [39], $Ba(OH)_2\cdot 8H_2O$, $Ba(ClO_4)_2\cdot 3H_2O$, $Ni(ClO_4)_2\cdot 6H_2O$, $Co(ClO_4)_2\cdot 6H_2O$, $Mn(ClO_4)_2\cdot 6H_2O$, $Mn(NO_3)_2\cdot 6H_2O$, $Cu(ClO_4)_2\cdot 6H_2O$, ZnI_2, $Zn(ClO_4)_2\cdot 6H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $CdCl_2\cdot 2{,}5H_2O$, $CdBr_2\cdot 4H_2O$, $Cd(NO_3)_2\cdot 4H_2O$ (160—320) [38], $Cd(ClO_4)_2\cdot 6H_2O$, $NaClO_3$, $NaClO_4\cdot H_2O$, $NaBO_3$, $NaSCN\cdot 2H_2O$, $Na_2CrO_4\cdot 4H_2O$, $NaB(OH)_4\cdot 2H_2O$, $NaBF_4$, $Na_3PO_4\cdot 12H_2O$, K_2CrO_4 (60—300) [41], $K_2Cr_2O_7$ (80—300) [41, 42], KIO_4, $CsNO_3$, $CsBrO_3$, $RbBrO_3$, $RbNO_3$, $AgBrO_3$, Ag_2SeO_3, Ag_2SeO_4, Ag_2MoO_4, Ag_2WO_4, $ScCl_3\cdot 6H_2O$, $UO_2SO_4\cdot 2.5H_2O$, $UF_4\cdot 2{,}5H_2O$, $ThF_4\cdot 2.5H_2O$.

Salts for which only measurement of the enthalpy of reaction (10) is required: $AlCl_3.6H_2O$, $NH_4Al(SO_4)_2.12H_2O$, $NH_4Cr(SO_4)_2.12H_2O$, $(NH_4)_2SnCl_6$, K_2SnCl_6.

Salts for which only measurements of $\gamma\pm$ and a_{H_2O} for m_{sat} are required: $FeSO_4.7H_2O$, Cs_2CrO_4, $SnCl_2.2H_2O$, $(NH_4)_2SiF_6$, Na_2SiF_6, $NaHCOO.2H_2O$.

In the determination of the entropies of crystalline hydrates it is necessary to take account of the fact that some of them have a residual entropy at 0 K. To determine this it is necessary to know the entropy of the anhydrous salt (or crystalline hydrates containing a smaller number of water molecules) and the enthalpy changes in the dehydration. The latter can be calculated if the dissociation pressures of the crystalline hydrates and the enthalpies of solution of the anhydrous salts and the crystalline hydrates in water to give solutions of the salt having the same concentration are known. Examples of these calculations can be found in papers dealing with the determination of the standard entropies of $Na_2SO_4.10H_2O$,[43] $Na_2CO_3.10H_2O$,[44] $Na_2HPO_4.12H_2O$,[45] $ZnF_2.4H_2O$,[46] $ZnSO_4.7H_2O$,[47] etc.

The second group consists of salts for which two types of experimental study are required, namely:

a) ΔH°_{298} for reaction (10); $\gamma\pm$ and a_{H_2O} for m_{sat}—for Cs_2MoO_4, SnI_2, $SnSO_4$, NaN_3.

b) ΔS°_{298}; $\gamma\pm$ and a_{H_2O} for m_{sat}—for K_2SeO_3, K_2SeO_4, $Na_2SeO_3.5H_2O$, $Na_2TeO_3.5H_2O$, Li_2TeO_3, $CaSeO_4.2H_2O$, $NaVO_3.2H_2O$, $NpO_2(NO_3)_2.6H_2O$, $PuCl_3.6H_2O$, K_2PdCl_4, K_2PtCl_4.

c) ΔH°_{298} for reaction (10); S°_{298}—for $Cr(NO_3)_3.9H_2O$, $Cr_2(SO_4)_3.18H_2O$, $K_3PO_4.7H_2O$, $K_2HPO_4.3H_2O$, $K_4P_2O_7.3.5H_2O$, $Na_2SO_4.7H_2O$, α-$NaH_2AsO_4.H_2O$, $K_3AsO_4.7H_2O$, $K_2HAsO_4.3H_2O$, $Na_3AsO_4.8H_2O$, $NaCN.2H_2O$, $Na_2SiO_3.9H_2O$, $Na_2GeO_3.7H_2O$.

Finally, for salts of the third group there are no thermodynamic data making it possible to characterise reaction (10), except the concentration of the saturated solution, and for these, the measurement of all three properties is required: $NaIO_4.3H_2O$, $H_2TeO_4.2H_2O$, $U(SO_4)_2.8H_2O$, $Th(SO_4)_2.9H_2O$, $Zr(SO_4)_2.4H_2O$, $CrSO_4.7H_2O$, $Sc(NO_3)_3.4H_2O$, $Na_2H_2PO_3.2.5H_2O$, KVO_3, α-$Na_3VO_4.12H_2O$, $UO_2CrO_4.5.5H_2O$, $Bi(NO_3)_3.5H_2O$, $Hg(ClO_4)_2.6H_2O$, $Na_2.MoO_4.2H_2O$, $Na_2WO_4.2H_2O$.

In the field of high-temperature studies, it is desirable to obtain more accurate values for the enthalpies of sublimation of a number of elements (for example, Ge, B, Zr, U, Re, Tc, Si, Be, Al, and the actinides), to study the energies of dissociation and enthalpies of formation of gaseous As_4, As_2, Sb_4, Sb_2, Tc_2, Se_2, N_2, and O_2, and to study the spectra of atoms with incomplete electron levels (transition metals, lanthanides, actinides) to determine the types of ground electronic states and the energies of the low electronic states.

The thermodynamic studies proposed above, which should lead to a significant increase in the accuracy of key quantities, is of course to some extent subjective and incomplete, and may be extended considerably. The present authors hope that experimentalists in the field of thermodynamics will consider precise studies of the above substances.

III. APPENDIX

Key Thermodynamic Quantities Recommended by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions§

Substance	State	ΔH^0_{298}, kJ mole^{-1}	S^0_{298}, J K^{-1} mole^{-1}	$H^0_{298}-H^0(0)$, kJ mole^{-1}
O	gas	249.17±0.10	160.946±0.020	6.728±0.003
O_2	gas	0	205.037±0.033	8.682±0.004
H	gas	217.997±0.006	114.604±0.015	6.197±0.002
H^+	aq	0	0	—
H_2	gas	0	130.570±0.033	8.468±0.003
OH^-	aq	−230.025±0.045	−10.71±0.20	—
H_2O	liquid	−285.830±0.042	69.950±0.080	13.293±0.020
H_2O	gas	−241.814±0.042	188.724±0.040	9.908±0.008
He	gas	0	126.039±0.012	6.197±0.002
Ne	gas	0	146.214±0.016	6.197±0.002
Ar	gas	0	154.732±0.020	6.197±0.002
Kr	gas	0	163.971±0.020	6.197±0.002
Xe	gas	0	169.573±0.020	6.197±0.002
F	gas	79.39±0.30	158.640±0.020	6.518±0.004
F^-	aq	−333.35±0.65	−13.18±0.54	—
F_2	gas	0	202.685±0.040	8.825±0.004
HF	gas	−273.30±0.70	173.665±0.035	8.599±0.004
Cl	gas	121.302±0.008	165.076±0.020	6.272±0.003
Cl^-	aq	−167.080±0.088	56.73±0.16	—
Cl_2	gas	0	222.965±0.040	9.180±0.008
HCl	gas	−92.31±0.13	186.786±0.033	8.640±0.004
Br	gas	111.86±0.12	174.904±0.020	6.197±0.020
Br	aq	−121.50±0.15	82.84±0.20	—
Br_2	liquid	0	152.210±0.040	24.52±0.13
Br_2	gas	30.91±0.11	245.350±0.054	9.724±0.012
HBr	gas	−36.38±0.17	198.585±0.033	8.648±0.004
I	gas	106.762±0.040	180.673±0.020	6.197±0.002
I^-	aq	−56.90±0.84	106.70±0.20	—
I_2	crystalline	0	116.139±0.080	13.196±0.040
I_2	gas	62.421±0.080	260.567±0.063	10.117±0.021
HI	gas	26.36±0.80	206.480±0.040	8.657±0.006
S	crystalline, orthorhombic	0	32.054±0.050	4.412±0.060
S	gas	276.98±0.25	167.715±0.035	6.657±0.004
S_2	gas	128.49±0.30	228.055±0.050	9.131±0.008
SO_2	gas	−296.81±0.20	248.11±0.06	10.548±0.013
SO_4^{2-}	aq	−909.60±0.40	18.83±0.50	—
N	gas	472.68±0.40	153.189±0.020	6.197±0.002
N_2	gas	0	191.502±0.025	8.669±0.003
NO_3^-	aq	—	146.94±0.85	—
NH_3	gas	−45.94±0.35	192.67±0.08	10.046±0.008
NH_4^+	aq	−133.26±0.25	111.17±0.75	—
P	crystalline, white	0	41.09±0.25	5.360±0.015
P	gas	316.5±1.0	163.085±0.020	6.197±0.002
P_2	gas	144.0±2.0	218.01±0.04	8.903±0.008
P_4	gas	58.9±0.3	279.9±0.5	14.10±0.24
C	crystalline, graphite	0	5.74±0.12	1.050±0.020
C	gas	716.67±0.44	157.988±0.020	6.535±0.006
CO	gas	−110.53±0.17	197.556±0.032	8.673±0.008
CO_2	gas	−393.51±0.13	213.677±0.040	9.364±0.008
Si	crystalline	0	18.81±0.08	3.217±0.008
Si	gas	450±8	167.870±0.035	7.550±0.004
SiO_2	α-quartz	−910.7±1.0	41.46±0.20	6.916±0.020
SiF_4	gas	−1614.95±0.85	282.65±0.40	15.36±0.05
Ge	crystalline, cubic	0	31.09±0.13	4.636±0.015
GeO_2	crystalline, tetragonal	−580.2±1.2	39.71±0.15	7.230±0.020
GeF_4	gas	−1190.15±0.50	301.8±1.0	17.30±0.08
Sn	crystalline, white	0	51.18±0.08	6.323±0.008
Sn	gas	301.2±1.7	168.380±0.020	6.215±0.002
Sn^{2+}	aq	−8.9±0.8	−15.8±4.0	—
SnO	crystalline	−285.93±0.70	57.17±0.30	8.736±0.022
SnO_2	crystalline	−580.78±0.40	52.3±1.2	8.76±0.08
Pb	crystalline	0	64.80±0.30	6.870±0.020
Pb	gas	195.20±0.80	175.270±0.020	6.197±0.002
Pb^{2+}	aq	0.92±0.25	17.7±0.8	—
$PbSO_4$	crystalline	−919.94±0.90	148.49±0.40	20.050±0.040
B	crystalline	0	5.90±0.08	1.222±0.008
B	gas	560±12	153.325±0.035	6.315±0.004
B_2O_3	crystalline	−1273.5±1.4	53.97±0.30	9.301±0.040
BF_3	gas	−1135.95±0.80	254.31±0.10	11.650±0.020
Al	crystalline	0	28.35±0.08	4.565±0.010
Al	gas	329.7±4.0	164.440±0.030	6.919±0.004
Al_2O_3	α-corundum	−1675.7±1.3	50.92±0.10	10.016±0.020
AlF_3	crystalline	−1510.4±1.3	66.5±0.4	11.62±0.04
Zn	crystalline	0	41.63±0.13	5.657±0.020
Zn	gas	130.42±0.20	160.875±0.025	6.197±0.002

Key Thermodynamic Quantities (continued)

Substance	State	ΔH^0_{298}, kJ mole^{-1}	S^0_{298}, J K^{-1} mole^{-1}	$H^0_{298}-H^0(0)$, kJ mole^{-1}
Zn^{2+}	aq	−153.39±0.20	−109.6±0.7	—
ZnO	crystalline	−350.46±0.27	43.64±0.40	6.933±0.040
Cd	crystalline	0	51.80±0.15	6.247±0.004
Cd^{2+}	aq	−75.88±0.60	−72.8±1.2	—
CdO	crystalline	−258.1±0.8	54.8±1.7	8.41±0.08
$CdSO_4 \cdot {}^8/_3\ H_2O$	crystalline, monoclinic	−1729.55±0.80	229.66±0.40	35.56±0.04
Hg	liquid	0	75.90±0.12	9.342±0.008
Hg	gas	61.38±0.04	174.860±0.020	6.197±0.002
Hg^{2+}	aq	170.16±0.20	−36.32±0.80	—
Hg_2^{2+}	aq	166.82±0.20	65.52±0.80	—
HgO	crystalline, red	−90.83±0.12	70.25±0.30	9.117±0.025
Hg_2Cl_2	crystalline	−265.45±0.30	191.6±1.5	23.35±0.20
Hg_2SO_4	crystalline	−743.41±0.50	200.71±0.20	26.070±0.030
Cu	gas	0	33.15±0.08	5.004±0.008
Cu	aq	337.6±1.2	166.285±0.025	6.197±0.002
Cu^{2+}	crystalline	65.69±0.80	−97.1±1.2	—
$CuSO_4$	crystalline	−771.1±1.2	109.2±0.4	16.86±0.08
Ag	gas	0	42.55±0.21	5.745±0.020
Ag	aq	284.9±0.8	172.883±0.025	6.197±0.002
Ag^+	crystalline	105.750±0.085	73.38±0.40	—
AgCl	crystalline	−127.070±0.085	96.23±0.20	12.033±0.040
Th	gas	0	53.39±0.40	6.510±0.020
Th	crystalline	598±6	190.06±0.04	6.197±0.002
ThO_2	crystalline	−1226.4±3.5	65.23±0.20	10.560±0.020
U	crystalline	0	50.20±0.20	6.364±0.020
UO_2	aq	−1085.0±1.0	77.03±0.20	11.280±0.020
UO_2^{2+}	crystalline (γ)	−1019.2±2.5	−98.3±4.0	—
UO_3	crystalline	−1223.8±2.0	96.11±0.40	14.585±0.080
U_3O_8	crystalline	−3574.8±2.5	282.55±0.50	42.74±0.10
Be	gas	0	9.50±0.08	1.950±0.020
Be	crystalline	324±5	136.165±0.020	6.197±0.002
BeO	crystalline	−609.4±2.5	13.77±0.04	2.837±0.008
Mg	gas	0	32.68±0.10	5.000±0.030
Mg	crystalline	147.10±0.80	148.535±0.020	6.197±0.002
MgO	crystalline	−601.5±0.3	26.95±0.15	5.160±0.020
MgF_2	gas	−1124.2±1.2	57.2±0.4	9.92±0.06
Ca	aq	0	41.6±0.4	5.73±0.04
Ca	crystalline	177.8±0.8	154.775±0.020	6.197±0.002
Ca^{2+}	crystalline	−543.10±0.80	−56.4±0.4	—
CaO	aq	−635.09±0.90	38.1±0.4	6.75±0.06
Li	crystalline	0	29.12±0.20	4.632±0.040
Li^+	aq	−278.455±0.090	11.30±0.35	—
Na	crystalline	0	51.30±0.20	6.460±0.020
Na^+	aq	−240.300±0.065	58.41±0.20	—
K	crystalline	0	64.68±0.20	7.088±0.020
K^+	aq	−252.17±0.10	101.04±0.25	—
Rb	crystalline	0	76.78±0.30	7.489±0.020
Rb^+	aq	−251.12±0.13	120.46±0.40	—
Cs	crystalline	0	85.23±0.40	7.711±0.020
Cs^+	aq	−258.04±0.13	132.84±0.40	—

§ The recommended values were prepared by the International Task Group of CODATA for Key Thermodynamic Quantities: J. B. Cox (Present President of the Group), J. Drowart, L. V. Gurvich, V. A. Medvedev, J. B. Pedley, S. Sunner, D. D. Wagman, L. G. Hepler, and W. H. Evans. From the Soviet Union, the following also took part in this work: G. A. Bergman, V. P. Vasil'ev, A. F. Vorob'ev, G. L. Gal'chenko, V. P. Kolesov, I. L. Khodakovskii, and V. S. Yungman. The Table includes material published in CODATA Bullentins (see Ref. 48), including Bulletins[49,50] published after the Seventh All Union Conference. In addition to the above CODATA Bulletins and other publications[5,6], more detailed and complete information on key thermodynamic quantities, including commentaries, bibliographies, atomic weights, energy units, etc. will be published in a special information bulletin being prepared by the State Standard Reference Data Service of Gosstandardt SSSR (USSR State Standards).

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