High-Temperature Mass Spectrometry: Instrumental Techniques, Ionization Cross-Sections, Pressure Measurements, and Thermodynamic Data (IUPAC Technical Report)

Jean Drowart, Christian Chatillon, John Hastie, and David Bonnell

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Determination of thermodynamic properties at high temperatures for condensed phases, and for gaseous or vapor species, by mass spectrometric (MS) study of vaporization processes has been performed for 50 years. During this period, a number of review papers have appeared describing instruments and experimental procedures in high-temperature mass spectrometry (HTMS). Synopses of the results have also been presented. Data obtained by this technique for individual compounds, whether gaseous or in the condensed phase, are incorporated in tabulations of dissociation energies, of thermodynamic properties, and of ionization potentials. A key aspect of the method is the conversion of primary mass spectral ion intensity data for individual species at specified temperatures to absolute or relative partial pressures.

The purpose of this report is to assess the accuracy and precision of pressures obtained from MS measurements. Attention is paid to the influence of ionization cross-sections and of other factors on such data. The report summarizes experimental, calculated, and estimated cross-sections for ionization of atoms and inorganic molecules typically present in high-temperature vapors.

Experimental cross-sections determined for some 56 atoms are generally close to theoretically calculated values, especially when excitation—autoionization is taken into account. Absolute or relative cross-sections for formation of parent ions were measured for ca. 100 molecules. These include homonuclear diatomic and polyatomic molecules, oxides, chalcogenides, halides, and hydroxides. Additivity of atomic cross-sections supplemented by empirical corrections provides fair estimates of molecular cross-sections. Causes of uncertainty are differences in interatomic distances and in shapes of potential energy curves (surfaces) of neutral molecules and of molecular ions and tendency toward dissociative ionization in certain types of molecules. Various mass spectrometric procedures are described that render the accuracy of measured thermodynamic properties of materials largely independent of ionization cross-sections. This accuracy is comparable with that of other techniques applicable under the conditions of interest, but often only the mass spectrometric procedure is appropriate at high temperatures.

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Chemical Speciation of Environmentally Significant Heavy Metals with Inorganic Ligands. Part 1: The Hg^{2+}- Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} Aqueous Systems (IUPAC Technical Report)

Kipton J. Powell, Paul L. Brown, Robert H. Byrne, Tamás Gajda, Glenn Hefter, Staffan Sjöberg, and Hans Wanner

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This document presents a critical evaluation of the equilibrium constants and reaction enthalpies for the complex formation reactions between aqueous Hg(II) and the common environmental inorganic ligands Cl^-, OH^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}. The analysis used data from the IUPAC Stability Constants database, *SC-Database*, focusing particularly on values for 25°C and perchlorate media. Specific ion interaction theory (SIT) was applied to reliable data available for the ionic strength range $I_c \leq 3.0$ mol dm^{-3}.

Recommended values of $\log_{10} \beta_{p,q,r}^{\circ}$ and the associated reaction enthalpies, $\Delta_r H_m^{\circ}$, valid at $I_m = 0$ mol kg^{-1} and 25°C, were obtained by weighted linear regression using the SIT equations. Also reported are the equations and specific ion interaction coefficients required to calculate $\log_{10} \beta_{p,q,r}$ values at higher ionic strengths and other temperatures. A similar analysis is reported for the reactions of H^+ with CO_3^{2-} and PO_4^{3-}. Diagrams are presented to show the calculated distribution of Hg(II) amongst these inorganic ligands in model natural waters. Under typical environmental conditions, Hg(II) speciation is dominated by the formation of $HgCl_2$(aq), Hg(OH)Cl(aq), and $Hg(OH)_2$(aq).

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