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Thermodynamic Properties of the Aqueous Ba^{2+} Ion and the Key Compounds of Barium

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Recommended thermochemical property values, $\Delta_f H^\circ$, $\Delta_f G^\circ$ and S° for the aqueous ion of barium, Ba^{2+} , are given at 298.15 K in SI units. The values are: $\Delta_f H^\circ = -534.64 \pm 1.80 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f G^\circ = -557.60 \pm 1.81 \text{ kJ}\cdot\text{mol}^{-1}$ and $S^\circ = 8.80 \pm 0.50 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$. They are consistent with the CODATA Key Values for Thermodynamics. The evaluation involves the analysis of the enthalpy changes, Gibbs energy changes, and the entropy measurements for all key substances in the key network. A consistent set of thermochemical property values is given for $\text{BaO}(\text{cr})$, $\text{BaH}_2(\text{cr})$, $\text{BaCl}_2(\text{cr})$, $\text{BaCl}_2\cdot 2\text{H}_2\text{O}(\text{cr})$, $\text{Ba}(\text{NO}_3)_2(\text{cr})$, and $\text{BaCO}_3(\text{cr, witherite})$, as well as reconstituted recommended process values with uncertainties for reactions involving these substances. ©1995 American Institute of Physics and American Chemical Society.

Key words: aqueous Ba^{2+} , barium compounds, CODATA, data evaluation, enthalpy, entropy, Gibbs energy, key compounds, key values, thermochemical measurements.

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1. Introduction

1.1. Purpose

The present paper is concerned with the evaluation and selection of the thermochemical properties of the aqueous ion Ba^{2+} and with those key compounds that are in the "key network." The properties studied are Δ_fH° , Δ_fG° , and S° at 298.15 K, all in SI units. All values are consistent with the CODATA Key Values [89COX/WAG].^a

There has been no complete reevaluation of the key network of Ba compounds that leads to the above mentioned property values of the $\text{Ba}^{2+}(\text{ao})$ and the key compounds on the CODATA scale that also incorporates the more recent data.

The property values given in the review by 69PAR, 71PAR/WAG (82WAG/EVA) need to be updated in consideration of the more recent experimental measurements which cast doubt on some of the selected values (e.g. $\Delta_fH^\circ(\text{BaO}, \text{cr})$ by 73FIT/HUB differs by more than five $\text{kJ} \cdot \text{mol}^{-1}$ from the selection in the review) and also cannot easily be used with the CODATA Key Values [89COX/WAG]. The 79MED/BER and 79ROB/HEM evaluations are also not compatible with the CODATA selections although they contain the more current $\Delta_fH^\circ(\text{BaO}, \text{cr})$. Also, as pointed out by 86BUS/PLU, some calculated process values, such as for $\Delta_{\text{sol}}G^\circ(\text{BaCO}_3, \text{cr}, \text{siderite})$ do not agree (within the stated uncertainty) with the more recent experimental values. 86BUS/PLU offer preliminary values for Δ_fG° , Δ_fH° , and S° for $\text{BaCO}_3(\text{cr})$, $\text{BaO}(\text{cr})$, and $\text{Ba}^{2+}(\text{ao})$ on the CODATA scale, but base their $\Delta_{\text{sol}}H^\circ(\text{BaCl}_2, \text{cr})$ and their $(\Delta_fH^\circ(\text{BaO}, \text{cr}) - \Delta_fH^\circ(\text{BaCl}_2, \text{cr}))$

on 71PAR/WAG. Recently, 90COR/KON present values on the CODATA scale, but only for Δ_fH° 's for $\text{Ba}^{2+}(\text{ao})$, $\text{BaO}(\text{cr})$, and $\text{BaCl}_2(\text{cr})$. A review and analysis are then appropriate.

1.2. Conventions and Auxiliary Data

1.2.1. Definitions and Symbols

The recommendations of the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry [82IUP] are followed for thermodynamic conventions, standard states, terminology, nomenclature, symbols, and units. The symbols used here are also given in 89COX/WAG.

For aqueous solutions the following symbols and definitions from 65PAR are used:

- ϕ_L = the relative apparent molal enthalpy of the solute or $-\Delta_{\text{dil}}H (m \rightarrow 0)$, an integral quantity;
- L_1 = the relative partial molal enthalpy of the solvent in the given solution; and,
- L_2 = the relative partial molal enthalpy of the solute in the given solution.

In addition, in order to maintain the same symbols in the text as in a computer based reaction catalog, the following are used:

- ai = hypothetical standard state, $m = 1$ for an electrolyte in aqueous solution (the sum of the values for the ions);
- ao = hypothetical standard state, undissociated;
- aq = aqueous, unspecified concentration, usually dilute; 250 H_2O , etc. = solution of specified composition; and,
- D = differential (partial molar property).

1.2.2. Reference States

The reference states used are as given in 89COX/WAG.

1.2.3. Molar Masses

The molar masses used are consistent with the relative atomic masses recommended by 86IUP and given in 88MIL/CVI.

1.2.4. Units, Fundamental Constants, and Thermochemical Property Values for Auxiliary Data

All values in the tables are given in SI units as recommended by 82IUP. Thermochemical property and process values cited in the text are at 298.15 K unless otherwise specified and are given as, e.g., Δ_fH° , rather than $\Delta_fH^\circ (298.15 \text{ K})$.

Values for the fundamental constants are taken from 86COH/TAY (see 88MIL/CVI for consolidated IUPAC Physical Chemistry units, etc.).

^aThis is a reference code used in the text and in computer-based reaction catalogs. It is keyed to the bibliographic references given in Sec. 11. A description of the reference code is given in Sec. 1.2.5.

The primary source for all thermochemical property values is 89COX/WAG which gives the CODATA Key Values for Thermodynamics; those used here will not be repeated. Citation to readily available literature values consistent with CODATA selections will be made. For example, use is made of the compilation 82WAG/EVA for those processes not defined by CODATA where the processes are independent of the selected property values, such as ϕ_L for HCl(aqueous), HNO₃(aqueous) (see also 65PAR). Those values not readily available will be given here.

1.2.5. Description of Bibliographic References

In order to use the same reference citation in the text as in a computer based reaction catalog, a reference code is used. The citation is given as follows:

The final two digits of the year (nineteenth century citations carry four digits for the year) precedes the first three letters of the first two author's last names (separated by a slash) in upper case letters. A number at the end of the code indicated that there is more than one reference having the same first two authors codes and year of publication.

The Bibliography in Sec. 11 is arranged chronologically by this reference code and alphabetically by the first author within each year. A full reference, including all authors, journal volume, page, and year of publication accompanies each reference code. Protocols for the computer format for entering references into the bibliography have been prepared by 83NEU.

1.2.6. Uncertainties

The uncertainties in the values for reactions given in the analysis and used in the text are initial uncertainties assumed by the evaluator, as discussed in 87PAR/EVA and may or may not agree with the experimentalist's appraisal. In the course of the evaluation and in rationalizing the property values of a substance from the various measurement paths and from replicate measurements of the same path, this initial judgment may prove to be unrealistic. The uncertainties listed in the tables of recommended property values for the substances are the evaluator's final estimate of the reliability of the predicted value. Use of these uncertainties, however, to calculate the uncertainty of a process value (as the square root as the sum of squares of all the uncertainties in the properties of the substances in the process) may result in too high a value since (1) the assigned uncertainty on the property value incorporates the uncertainties on the process values from which it is derived and (2) the property values of the substances in the process could be highly correlated. In order to avoid this, the recommended reconstituted process values for the processes of interest are tabulated with the evaluator's estimated reliability (assumed to have a level of confidence of 95%).

1.3. Method of Approach

1.3.1. General

The sequential method, as described by 76GAR/PAR and 77GAR/PAR, is used. In this method all of the data on the

compounds of interest in the network of the elements are assembled and the properties [$\Delta_f H^\circ$, $\Delta_f G^\circ$, and S°] are calculated and evaluated compound by compound, starting with the compounds whose properties can be determined independently, that is, they depend only on known auxiliary data (in this case, CODATA Key Values [89COX/WAG] and CODATA compatible values) and not on any other compounds of the same element. Then the properties of other compounds dependent on the first selections are set. If several measurement paths involve the same compound, a confirmation of the choice may be obtained. If the confirmation of the choice (within the stated uncertainty) is not obtained, a *reworking* of the previous selections may be made and revised values selected in order to receive a reasonable over-all fit. This manual sequential method is iterative. More than one pass is involved in establishing the final values for the key compounds in the key network. In order to show the evolution to the final recommended values in the evaluation I indicate in each section the initial selection, that is, the *tentative* or *working* value, and its modification as I proceed in the evaluation to test, rationalize or modify, and finalize the recommendations. So that the user will understand this, I also indicate in each section what the final *resolved* recommendations will be.

1.3.2. The Systematic Analysis

The major compounds in the key network for the determination of the properties of Ba²⁺(ao) are BaO(cr), BaH₂(cr), BaCl₂(cr), BaCl₂·2H₂O(cr), Ba(NO₃)₂(cr) and BaCO₃(cr). The various parameters to be considered are:

1. The $\Delta_f H^\circ$ (BaO,cr) from direct oxidation of Ba(cr) and also from the $\Delta_{sol} H^\circ$ (Ba,cr) and $\Delta_{sol} H^\circ$ (BaO,cr) in aqueous HCl.
2. The $\Delta_f H^\circ$ (BaCl₂,cr) from measurements of $\Delta_{sol} H^\circ$ (Ba,cr) and $\Delta_{sol} H^\circ$ (BaCl₂,cr) in HCl, and from $\Delta_{sol} H^\circ$ (BaO,cr) in aqueous HCl.
3. The $\Delta_f H^\circ$ (BaH₂,cr) from measurements of $\Delta_{sol} H^\circ$ (Ba,cr) and $\Delta_{sol} H^\circ$ (BaH₂,cr) in aqueous HCl, and also from the direct enthalpy of hydrogenation of Ba(cr) and the link to $\Delta_f H^\circ$ (BaCl₂,cr).
4. The $\Delta_{sol} H^\circ$ (BaCl₂,cr) from measurements in H₂O and from measurements in aqueous HCl as a function of the concentration of HCl.
5. The $\Delta_f H^\circ$ (BaCO₃,cr) from (1) the $\Delta_{sol} H^\circ$ (BaO,cr) and $\Delta_{sol} H^\circ$ (BaCO₃,cr) in HCl and (2) the $\Delta_{decomp} H^\circ$ (BaCO₃,cr).
6. The $\Delta_{sol} S^\circ$ of BaCl₂·2H₂O(cr), Ba(NO₃)₂(cr), and BaCO₃(cr) calculated from the $\Delta_{sol} H^\circ$ and $\Delta_{sol} G^\circ$ of the above salts. With the measured S° values of these salts and the CODATA S° values for Cl⁻(ao), NO₃⁻(ao), and CO₃²⁻(ao) we calculate S° for Ba²⁺(ao).
7. Values for $\Delta_f H^\circ$ (Ba²⁺,ao) are obtained from (1) BaCl₂(cr), $\Delta_f H^\circ$ and $\Delta_{sol} H^\circ$ in H₂O, (2) the same from BaCO₃(cr), (3) the same from Ba(NO₃)₂(cr).

The various values for $\Delta_f H^\circ$ (Ba²⁺,ao) and S° (Ba²⁺,ao) are reconciled and smoothed to obtain final property values for the ion and all substances in the key network.

The recommended values for the various processes are reconstituted from the tabulated property values.

2. The Enthalpy of Formation of BaO(cr)

2.1. From Direct Combustion

63MAH reported the direct enthalpy of combustion of Ba(cr) to BaO(cr) at 303.15 K to be -581.83 ± 2.93 kJ·mol⁻¹. Corrected to 298.15 K with essentially a negligible $\Delta C_p = +0.004$ kJ·K⁻¹·mol⁻¹, we have



2.2. From Measurements of the Enthalpies of Reaction of Ba(cr) and BaO(cr) in Aqueous HCl Solutions

66FLI/KOV combined their measurements of $\Delta_{\text{sol}} H^\circ(\text{BaO}, \text{cr})$ with the measurements of $\Delta_{\text{sol}} H^\circ(\text{Ba}, \text{cr})$ by 23GUN/BEN^b, citing the following corrections to the 23GUN/BEN measurements, -0.42 kJ·mol⁻¹ for the difference in final concentrations of BaCl₂, -0.71 kJ·mol⁻¹ for the difference in concentration of HCl, and -1.21 kJ·mol⁻¹ for the temperature difference, to obtain from the combination of the following two reactions:

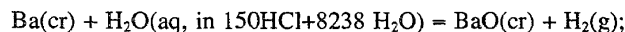
1. $\text{Ba}(\text{cr}) + 2\text{HCl}(\text{aq}) = \text{BaCl}_2(\text{aq, in HCl}) + \text{H}_2(\text{g}); \Delta H = -539.82 \text{ kJ}\cdot\text{mol}^{-1};$
2. $\text{BaO}(\text{cr}) + 2\text{HCl}(\text{aq}) = \text{BaCl}_2(\text{aq, in HCl}) + \text{H}_2\text{O}(\text{l}); \Delta H = -272.96 \text{ kJ}\cdot\text{mol}^{-1}.$

To yield:

3. $\text{Ba}(\text{cr}) + \text{H}_2\text{O}(\text{l}) = \text{BaO}(\text{cr}) + \text{H}_2(\text{g}); \Delta H^\circ = -266.86 \pm 0.84 \text{ kJ}\cdot\text{mol}^{-1}.$

This results in $\Delta_f H^\circ(\text{BaO}, \text{cr}) = -552.69 \pm 2.0$ kJ·mol⁻¹.

More recently 73FIT/HUB measured the $\Delta_{\text{sol}} H^\circ$ of both Ba(cr) (-535.34 ± 1.7 kJ·mol⁻¹) and BaO(cr) (-273.17 ± 0.96 kJ·mol⁻¹) in a 1.002 M HCl solution such that



$$\Delta H = -262.17 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}.$$

With $\Delta_f H^\circ(\text{H}_2\text{O, aq in } 150 \text{HCl} + 8238 \text{H}_2\text{O}) = -285.836 \pm 0.040$ kJ·mol⁻¹, $\Delta_f H^\circ(\text{BaO}, \text{cr}) = -548.01 \pm 2.0$ kJ·mol⁻¹.

90COR/KON repeated the $\Delta_{\text{sol}} H^\circ(\text{BaO}, \text{cr})$ (-273.08 ± 0.24 kJ·mol⁻¹) in a 1.0109 M HCl solution. Minor corrections were made to the exact condition used by 73FIT/HUB (-0.03 kJ·mol⁻¹) so that $\Delta H = -273.11 \pm 0.25$ kJ·mol⁻¹. Combination of this value with 73FIT/HUB's measurements on Ba(cr) results in $\Delta H^\circ = -262.23 \pm 1.72$ kJ·mol⁻¹ and $\Delta_f H^\circ(\text{BaO}, \text{cr}) = -548.07 \pm 1.72$ kJ·mol⁻¹, in excellent agreement with 73FIT/HUB.

The measured $\Delta_{\text{sol}} H^\circ(\text{Ba}, \text{cr})$ in the two studies differ by more than 4 kJ·mol⁻¹, far more than the variation of $\Delta_{\text{sol}} H^\circ(\text{BaO}, \text{cr})$. Sample purity of Ba(cr) may be the problem.

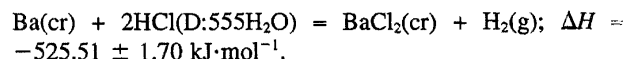
2.3. The Selected $\Delta_f H^\circ(\text{BaO}, \text{cr})$

The above measurements for $\Delta_f H^\circ(\text{BaO}, \text{cr})$ are: -581.85 ± 3.0 kJ·mol⁻¹ from the direct combustion, and from the $\Delta_{\text{sol}} H^\circ(\text{Ba}, \text{cr})$ and $\Delta_{\text{sol}} H^\circ(\text{BaO}, \text{cr})$ in HCl, -552.69 ± 2.0 , -548.01 ± 2.0 , -548.07 ± 1.72 kJ·mol⁻¹. The initial tentative selection is -548.04 ± 1.72 kJ·mol⁻¹. It also becomes the final selection.

3. The Enthalpy of Formation of BaCl₂(cr)

3.1. From Measurements of the Enthalpies of Reaction of Ba(cr) and BaCl₂(cr) in Aqueous HCl Solutions

63EHR/PEI measured $\Delta_{\text{sol}} H^\circ(\text{Ba}, \text{cr})$ (-538.48 ± 1.5 kJ·mol⁻¹) and $\Delta_{\text{sol}} H^\circ(\text{BaCl}_2, \text{cr})$ (-12.97 ± 0.08 kJ·mol⁻¹) in 0.1N HCl, such that the final solution contained 2500 mol H₂O/mol BaCl₂. For:



Using $L_2(\text{HCl:555H}_2\text{O}) = 0.812$ kJ·mol⁻¹ from 65PAR, $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -858.05 \pm 1.8$ kJ·mol⁻¹ is obtained.

3.2. From Enthalpy Measurements of BaCl₂(cr) and BaO(cr) in Aqueous HCl

90COR/KON measured the $\Delta_{\text{sol}} H^\circ(\text{BaCl}_2, \text{cr})$ (-8.858 ± 0.084 kJ·mol⁻¹) in a 1.0109 N HCl (HCl:53.8H₂O) solution as well as $\Delta_{\text{sol}} H^\circ(\text{BaO}, \text{cr})$ (-273.08 ± 0.24 kJ·mol⁻¹) in a 1.0109 N HCl solution [final concentration (HCl: 54.54 H₂O)]. Applying a correction of 0.09 kJ·mol⁻¹ for the variation of $\Delta_{\text{sol}} H^\circ(\text{BaCl}_2, \text{cr})$ with concentration of HCl, I obtain BaO(cr) + 2HCl(D:54.2H₂O)^c = BaCl₂(cr) + H₂O(aq)^c; $\Delta H = -264.13 \pm 0.25$ kJ·mol⁻¹

and $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) - \Delta_f H^\circ(\text{BaO}, \text{cr}) = -306.96 \pm 0.25$ kJ·mol⁻¹. This is consistent with 90COR/KON's $\Delta_f H^\circ(\text{BaO}, \text{cr}) = -548.07 \pm 1.72$, $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -855.03 \pm 1.72$ kJ·mol⁻¹, and is in fair agreement with 63EHR/PEI, considering the overlapping uncertainty intervals.

3.3. The Relationship Between $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ and $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$

In Sec. 5.3 a value for $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) - \Delta_f H^\circ(\text{BaH}_2, \text{cr}) = -679.30 \pm 2.1$ kJ·mol⁻¹ is obtained from 63EHR/PEI's measurements. If the direct determination of $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$ (hydrogenation enthalpy of Ba(cr)) = -190.08 ± 0.4 kJ·mol⁻¹ from 68VOR/MON is used (Sec. 5.2.), $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -869.47 \pm 2.2$ kJ·mol⁻¹.

^b23GUN/BEN measurements were at 280 K with an aqueous HCl solution of 0.40 mol·kg⁻¹.

^c $L_2(\text{HCl:54.2H}_2\text{O}) = 2.75$ kJ·mol⁻¹ and $L_1(\text{H}_2\text{O}) = -0.006$ kJ·mol⁻¹ from 65PAR.

3.4. The Selected $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$

The three above paths lead to widely different values. The initial tentative selection is $-855.00 \pm 1.73 \text{ kJ}\cdot\text{mol}^{-1}$. It will also become the final recommendation.

4. The Enthalpy of Formation of $\text{Ba}(\text{NO}_3)_2(\text{cr})$

The $\Delta_f H^\circ(\text{Ba}(\text{NO}_3)_2, \text{cr})$ is dependent upon the $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ through the measurements of 44YOU on the $\Delta_{\text{sol}} H(\text{BaCl}_2, \text{cr})$ ($-8.728 \pm 0.04 \text{ kJ}\cdot\text{mol}^{-1}$) and the $\Delta_{\text{sol}} H(\text{Ba}(\text{NO}_3)_2, \text{cr})$ ($41.606 \pm 0.07 \text{ kJ}\cdot\text{mol}^{-1}$) in aqueous 1 N HCl solutions ($m=1.022 \text{ mol}\cdot\text{kg}^{-1}$).

1. $\text{BaCl}_2(\text{cr}) = (\text{BaCl}_2 + 45.5\text{HCl} + 2474\text{H}_2\text{O})(\text{soln I}); \Delta H_1 = -8.728 \pm 0.04 \text{ kJ}\cdot\text{mol}^{-1}$;
2. $\text{Ba}(\text{NO}_3)_2(\text{cr}) + 45.5\text{HCl} + 2474\text{H}_2\text{O} = \text{Ba}(\text{NO}_3)_2 + 45.5\text{HCl} + 2474\text{H}_2\text{O} (\text{soln II}); \Delta H_2 = +41.606 \pm 0.07 \text{ kJ}\cdot\text{mol}^{-1}$;

He also measured:

3. $2(\text{HNO}_3 + 26.5\text{H}_2\text{O}) + \text{soln I} = \text{soln III}; \Delta H_3 = +0.481 \pm 0.08 \text{ kJ}\cdot\text{mol}^{-1}$; and,
4. $26.5\text{H}_2\text{O(l)} + \text{soln II} = \text{soln III}; \Delta H_4 = -0.473 \pm 0.04 \text{ kJ}\cdot\text{mol}^{-1}$.

where soln III is $\text{Ba}(\text{NO}_3)_2 + 47.5\text{HCl} + 2500.5\text{H}_2\text{O}$.

The summation $\Delta H_1 - \Delta H_2 + \Delta H_3 - \Delta H_4$ results in

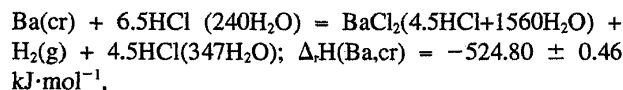
5. $\text{BaCl}_2(\text{cr}) + 2\text{HNO}_3(\text{in } 26.5\text{H}_2\text{O}) = \text{Ba}(\text{NO}_3)_2(\text{cr}) + 2\text{HCl(D:HCl} + 53.2\text{H}_2\text{O}); \Delta H_5 = -49.38 \pm 0.12 \text{ kJ}\cdot\text{mol}^{-1}$

The $\Delta_f H(\text{HNO}_3 \text{ in } 26.5 \text{ H}_2\text{O}) = -205.794 \pm 0.40 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta_f H(\text{D:HCl} + 53.2\text{H}_2\text{O}) = -164.36 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$ so that $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) - \Delta_f H^\circ(\text{Ba}(\text{NO}_3)_2, \text{cr}) = 132.25 \pm 0.43 \text{ kJ}\cdot\text{mol}^{-1}$. With the tentative $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -855.00 \pm 1.73$; $\Delta_f H^\circ(\text{Ba}(\text{NO}_3)_2, \text{cr}) = -987.25 \pm 1.80 \text{ kJ}\cdot\text{mol}^{-1}$. This tentative value will be modified in the smoothing process to the final $\Delta_f H^\circ = -988.02 \pm 1.80 \text{ kJ}\cdot\text{mol}^{-1}$.

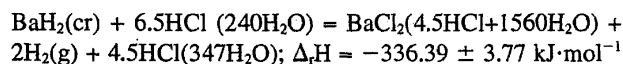
5. The Enthalpy of Formation of $\text{BaH}_2(\text{cr})$

5.1. From Measurements of the Enthalpies of Reaction of $\text{Ba}(\text{cr})$ and $\text{BaH}_2(\text{cr})$ in Aqueous HCl

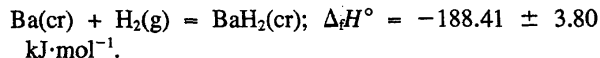
67VOR/MON obtained:



and



so that



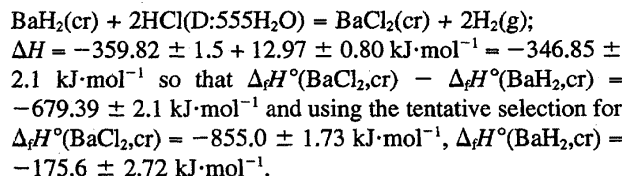
Previously 63EHR/PEI had used an aqueous solution of 0.1 N HCl (HCl:555 H₂O) so that the final BaCl₂ concentration was 2500 moles H₂O/mol BaCl₂, obtaining $\Delta H = -538.48 \pm 1.5$ and $-359.82 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively for the above reactions resulting in $\Delta_f H^\circ(\text{BaH}_2, \text{cr}) = -178.66 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$, in disagreement with the above.

5.2. From the Enthalpy of Hydrogenation of $\text{Ba}(\text{cr})$

68VOR/MON obtained $\Delta_f H^\circ = -190.08 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$ from 6 measurements, supporting their (67VOR/MON) value from measurements in HCl. See Sec. 5.1.

5.3. The Relationship Between $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ and $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$

Since 63EHR/PEI measured $\Delta_{\text{sol}} H(\text{BaCl}_2, \text{cr})$ ($-12.97 \pm 0.80 \text{ kJ}\cdot\text{mol}^{-1}$) in 0.1N HCl (see Sec. 3.1.) as well as $\Delta_{\text{sol}} H(\text{BaH}_2, \text{cr})$ (see Sec. 5.1.), one can also obtain



5.4. The Selected Value for $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$

The results differ widely for $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$. The selected value for $\Delta_f H^\circ(\text{BaH}_2, \text{cr}) = -177.0 \pm 4.9 \text{ kJ}\cdot\text{mol}^{-1}$ is based on the 63EHR/PEI measurements, since their measurements on $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ and $\Delta_{\text{sol}} H^\circ(\text{BaCl}_2, \text{cr})$ are in better agreement, i.e. more consistent with the values selected here for $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$, $\Delta_f H^\circ(\text{BaO}, \text{cr})$, and $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao})$ than a selection based on 68VOR/MON's measurements would be.

6. The Enthalpy of Formation of $\text{BaCO}_3(\text{cr})$ from the Decomposition to $\text{BaO}(\text{cr})$ and $\text{CO}_2(\text{g})$

6.1. From Solution Calorimetry

The measurements of 66ADA/CON on $\Delta_{\text{sol}} H$ of $\text{BaO}(\text{cr})$ ($-275.73 \pm 0.30 \text{ kJ}\cdot\text{mol}^{-1}$) and $\text{BaCO}_3(\text{cr})$ ($-6.49 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$) at 303.15 K in excess HCl ($m=4.35 \text{ mol}\cdot\text{kg}^{-1}$) saturated with $\text{CO}_2(\text{g})$ lead to



Since ΔC_p is negligible, ΔH° for this decomposition is $+269.24 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$.

Similarly 66GRE/PAS used HNO_3 -HF solutions at 323K to obtain $\Delta_{\text{sol}} H(\text{BaO}, \text{cr}) = -265.77 \pm 6.7 \text{ kJ}\cdot\text{mol}^{-1}$ and

$\Delta_{\text{sol}}H(\text{BaCO}_3, \text{cr}) = -21.25 \pm 0.9 \text{ kJ}\cdot\text{mol}^{-1}$ at 323 K. ΔH° for the decomposition = $244.5 \text{ kJ}\cdot\text{mol}^{-1}$ (the ΔC_p correction is considered negligible in the temperature range 323–298 K).

6.2. From the Vapor Pressure Measurements of $\text{CO}_2(\text{g})$ as a Function of T

81GUR/BER and 82CHA/AHM review and tabulate the available decomposition pressure data. Their calculations differ from each other because of the use of slightly different thermal functions for $\text{BaO}(\text{cr})$. The thermal functions accepted here for $\text{BaO}(\text{cr})$ from 85CHA/DAV are in agreement with 81GUR/BER. Hence the values tabulated by 81GUR/BER are reported here; additional sources given by 82CHA/AHM are corrected to the thermal functions used here and are included in Table 1.

Also included in it are the calorimetric measurements from 6.1.

TABLE 1. The $\Delta_{\text{decomp}}H^\circ(\text{BaCO}_3, \text{cr})$ at 298.15 K from vapor pressure measurements

Investigation	Temp. range, K	$\Delta H^\circ (\text{kJ}\cdot\text{mol}^{-1})$	
06FIN	1623	254.5	(3rd law)
51 LAN	1073–1477	287.5	(2nd law)
		272.5 ± 2.3	(3rd law)
69EVS/BUN	1203–1273	260.5	(2nd law)
		271.5	(3rd law)
76BAS/SIR	1031–1099	262.5	(2nd law)
		275.5	(3rd law)
	1160–1211	257.5	(2nd law)
		258.5	(3rd law)
Corrected from 82CHA/AHM			
05POT	1270–1470	245.3 ± 8.9	(3rd law)
16HED	1634	254.8	(3rd law)
27DUT	1375–1529	262.4 ± 2.7	(3rd law)
37HAC/WOL	1673	259.4	(3rd law)
From calorimetric measurements			
66ADA/CON	303.15	269.24 ± 1.1	
66GRE/PAS	323	244.5	

The vapor pressure measurements are discordant so that preference is given to the calorimetric measurement of 66ADA/CON, $\Delta H^\circ = 269.24 \text{ kJ}\cdot\text{mol}^{-1}$, although some weight is given to the 51LAN 3rd law $\Delta H^\circ = 272.5 \pm 2.3 \text{ kJ}\cdot\text{mol}^{-1}$ which shows a trend with temperature. The initial selection of $\Delta H^\circ = 269.24 \text{ kJ}\cdot\text{mol}^{-1}$ ($= -1210.79 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ for $\Delta_f H^\circ(\text{BaCO}_3, \text{cr})$) will be modified to the final recommended $\Delta H^\circ = 271.48 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\text{BaCO}_3, \text{cr}) = -1213.03 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ as a result of the rationalizing process.

7. The Thermodynamic Properties of $\text{Ba}^{2+}(\text{ao})$

7.1. The Enthalpy of Formation

7.1.1. The Standard Enthalpy of Solution of $\text{BaCl}_2(\text{cr})$

From measurements in H_2O

Table 2 lists the $\Delta_{\text{sol}}H^\circ$ (corrected to 298.15 K, where necessary) obtained from the various measurements. A reasonable tentative value for $\Delta_{\text{sol}}H^\circ(\text{BaCl}_2, \text{cr}) = -13.80 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$. The ϕ_L values used to correct to infinite dilution are from 71PAR/WAG and 82WAG/EVA. These ϕ_L values are based on the measurements of 31LAN/STR, 29RIC/DOL, 36SCH/COB, 66VOR/MON, 36SHI/TER, and 57TER.

TABLE 2. The $\Delta_{\text{sol}}H^\circ \text{BaCl}_2(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$ at 298.15 K

Investigator	Conc. $m, \text{mol}\cdot\text{kg}^{-1}$	$\Delta_{\text{sol}}H^\circ(m)$ $\text{kJ}\cdot\text{mol}^{-1}$	ΔH° $\text{kJ}\cdot\text{mol}^{-1}$
1875 BER	0.2413	-11.88^a	-14.06
1883 BER/ILO	0.2775	-10.95	-13.19
1888 THO	0.1387	-11.15	-13.08^b
04 BAU	0.125	-9.87^c	-12.76
08 SCH	0.1388	-8.46^d	-13.17
36 SCH/COB	0.1811	-11.18	-13.326
	to 1.444	to -10.67	
36 SHI/TER	0.0555	-11.90	-13.426
52 SAM	0.05	-11.88	-13.376
61CRI/COB	0.0018	-12.71	-13.347 ± 0.1
	to 0.01	to -13.01	
66VOR/MON	0.0185	-12.06	-13.065 ± 0.20
	to 0.0555	to -11.36	
68SAM/TSV	0.1110	-11.92	-13.753
69GRE/SNE	0.0156	-13.230	-13.393 ± 0.08
	to 0.0592	to -13.49	
73SMI/BER	0.011	e	-13.64 ± 0.13
77DAD/TAH	0.005	-12.853	-13.517 ± 0.10
	to 0.025	to -12.259	
78PER/THO	0.02	-13.01^f	-14.23 ± 0.22
83MON/ALE	0.003	-14.14	-14.234 ± 0.14
	to 0.019	to -14.29	
85JUI/TIS			-13.5
90COR/KON	0.0066	-13.069	-13.769 ± 0.06
		± 0.060	
90TAN/BAR			-13.50
Selected Value			-13.80 ± 0.10

^afrom 283 K, $\Delta C_p = -335 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^bfrom 291 K, $\Delta C_p = -356 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^cfrom 295 K, $\Delta C_p = -335 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^dfrom 290 K, $\Delta C_p = -347 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^ecites 71PAR/WAG.

^falso measured $\Delta_{\text{dil}}H$.

From Measurements in Aqueous HCl

Table 3 shows the measurements used to extrapolate to $\Delta_{\text{sol}}H^\circ(\text{BaCl}_2, \text{cr})$ from measurements in aqueous HCl . A value for $\Delta_{\text{sol}}H^\circ = -13.72 \pm 0.50 \text{ kJ}\cdot\text{mol}^{-1}$ is obtained in excellent agreement with the selected value obtained from measurements in H_2O . I is the ionic strength.

TABLE 3. The measurements of the $\Delta_{\text{sol}}H(\text{BaCl}_2, \text{cr})$ in aqueous HCl

$\text{BaCl}_2(\text{cr})$	$\Delta_{\text{sol}}H$ $\text{kJ}\cdot\text{mol}^{-1}$	$m \text{ BaCl}_2$ $\text{mol}\cdot\text{kg}^{-1}$	$m \text{ HCl}$ $\text{mol}\cdot\text{kg}^{-1}$	$\text{soln} \times (\text{HCl}+n\text{H}_2\text{O})^c$	I mol kg^{-1}	$\text{kJ}\cdot\text{mol}^{-1}$			
						$\Delta_{\text{D-H}}H^\circ$	$\Delta H'$	$\Delta H'$ graph	Predicted $\Delta_{\text{sol}}H$
44YOU	-8.728	0.022	1.051	47.5(a+52.8b)	1.117	-2.69	-11.42	-11.35	-8.66
50KAP/SAM	-7.20	0.030	1.90	63.4(a+29.21b)	1.99	-3.01	-10.21	-9.46	-6.45
63EHR/PEI	-12.97	0.022	0.0565	2.545(a+982b)	0.1225	-1.318	-14.29	-13.48	-12.16
52SAM	-8.62	0.045	0.899	19.98(a+61.7b)	1.034	-2.66	-11.28	-11.56	-8.90
	-7.99	0.045	1.24	27.56(a+44.8b)	1.375	-2.81	-10.81	-10.80	-7.99
	-6.49	0.045	1.83	40.67(a+30.3b)	1.965	-3.00	-9.49	-9.50	-6.50
90COR/KON	-8.858	0.0069	1.03	150(a+53.83b)	1.0507	-2.65	-11.51	-11.55	-8.90
	± 0.084								
76O'H/BOE	-9.94	0.005	~ 1.00	184(a+55.57b) ^d	1.037	-2.64	-12.58	-11.56	-8.92
	$\pm 0.07_5$								
Extrapolation this study									
		0	0		0			-13.72 ± 0.5	-13.80

^cComposition of solution converted to one mole of BaCl_2 in x moles of HCl where the $\text{H}_2\text{O}:\text{HCl}$ ratio is n . For convenience, HCl is given as a and H_2O as b .

^dContains one mole UO_2Cl_2 .

Table 4 shows the final recommended $\Delta_{\text{sol}}H^\circ(\text{BaCl}_2, \text{cr})$ as a function of I HCl where the concentration of BaCl_2 is very dilute.

TABLE 4. Recommended $\Delta_{\text{sol}}H^\circ(\text{BaCl}_2, \text{cr})$ in aqueous HCl

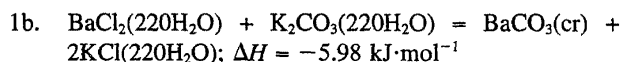
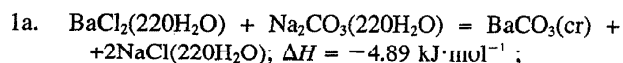
I HCl $\text{mol}\cdot\text{kg}^{-1}$	$\Delta H'$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H_{\text{D-H}}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{sol}}H$ $\text{kJ}\cdot\text{mol}^{-1}$
0.0	-13.80	0.0	-13.80
0.1	-13.50	-1.26	-12.24
0.2	-13.29	-1.63	-11.65
0.5	-12.65	-2.18	-10.47
1.0	-11.60	-2.62	-8.98
1.5	-10.52	-2.85	-7.67
2.0	-9.46	-3.01	-6.45

From Sec. 3.4, the initial tentative selection for $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -855.00 \pm 1.73 \text{ kJ}\cdot\text{mol}^{-1}$ with the selection for $\Delta_{\text{sol}}H^\circ = -13.80 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$ (from 7.111) results in $\Delta_f H^\circ(\text{BaCl}_2, \text{ai}) = -868.80 \pm 1.74 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao}) = -534.64 \pm 1.8 \text{ kJ}\cdot\text{mol}^{-1}$.

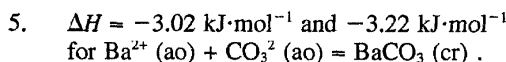
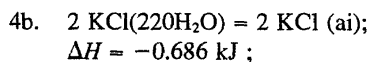
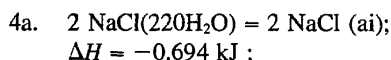
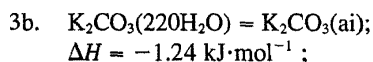
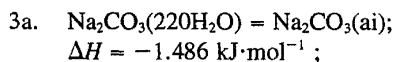
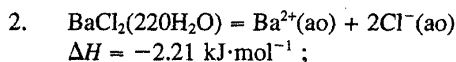
7.1.2. From the $\text{BaCO}_3(\text{cr})$ System

From the Calorimetric Enthalpy of Precipitation

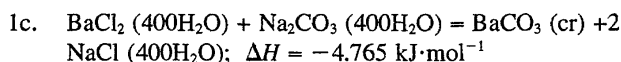
1875BER2 measured the enthalpy of reaction of aqueous BaCl_2 solutions ($\text{H}_2\text{O}/\text{BaCl}_2 = 220$) with aqueous Na_2CO_3 ($\text{H}_2\text{O}/\text{Na}_2\text{CO}_3 = 220$) and K_2CO_3 ($\text{H}_2\text{O}/\text{K}_2\text{CO}_3 = 220$) to precipitate $\text{BaCO}_3(\text{cr})$ at 289K, reporting $\Delta H = -6.02 \text{ kJ}\cdot\text{mol}^{-1}$ and $-7.11 \text{ kJ}\cdot\text{mol}^{-1}$. Corrected to 298K using $\Delta C_p = +0.125 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, the following are obtained:



Making use of ϕ_L from 82WAG/EVA for the following:



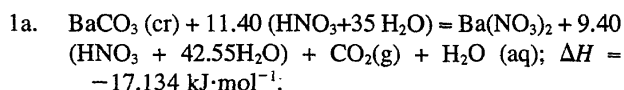
Similarly 1886THO measured the enthalpy of precipitation of $\text{BaCO}_3(\text{cr})$, from BaCl_2 ($\text{H}_2\text{O}/\text{BaCl}_2 = 400$) and Na_2CO_3 ($\text{H}_2\text{O}/\text{Na}_2\text{CO}_3 = 400\text{H}_2\text{O}$) at 291 K to be $-5.64 \text{ kJ}\cdot\text{mol}^{-1}$. With $\Delta C_p = +0.125 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, correction to 298 K results in



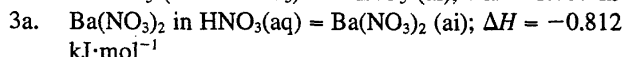
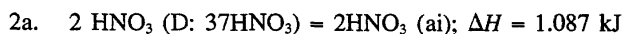
and using reactions analogous to 2–4 above, for species in 400 H_2O , with ΔH for 2c = $-1.937 \text{ kJ}\cdot\text{mol}^{-1}$, for 3c $-2.20 \text{ kJ}\cdot\text{mol}^{-1}$ and for 4c -0.726 kJ , $\Delta H^\circ(5) = -1.35 \text{ kJ}\cdot\text{mol}^{-1}$.

From the dissolution of $\text{BaCO}_3(\text{cr})$ in aqueous acid solutions

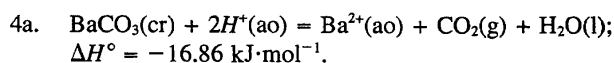
41ROT reported $\Delta H = -16.82 \text{ kJ}\cdot\text{mol}^{-1}$ at 293K which corrected to 298.15K (with $\Delta C_p = -0.063 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ results in:



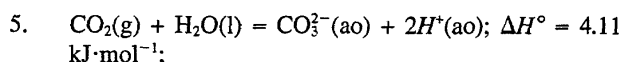
Using 82WAG/EVA for the following:



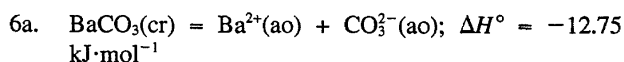
results in the following:



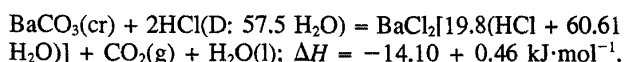
From 89COX/WAG (CODATA Key Values)



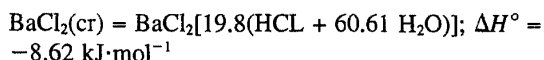
so that



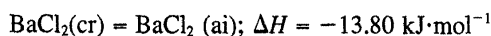
Similarly 54KAP/STA using aqueous HCl ($n\text{H}_2\text{O}/\text{HCl} = 55$) obtained



Using



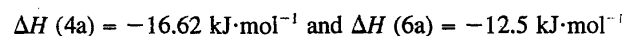
and



from Table 4 and



from 65PAR,



From Solubility Measurements as a Function of Temperature

The solubility of $\text{BaCO}_3(\text{cr})$ has been measured by 86BUS/PLU from 273.15K to 363.15K at 1 atm. They reported, from log K as a function of T , for the solution process at 298.15K $\Delta H = 2.94 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$.

The Selected $\Delta_{\text{sol}}H^\circ(\text{BaCO}_3, \text{cr})$ and $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao})$

Table 5 summarizes the values obtained for $\Delta_{\text{sol}}H^\circ$:

TABLE 5. $\text{BaCO}_3(\text{cr}) = \text{BaCO}_3(\text{ai})$

Investigator	$\Delta H^\circ, \text{kJ}\cdot\text{mol}^{-1}$	Method
1875BER2	+3.02	from pptn., Na_2CO_3
	+3.22	from pptn., K_2CO_3
1886THO	+1.35	from pptn., Na_2CO_3
41ROT	-12.75	soln with HNO_3
54KAP/STA	-12.5	soln with HCl
86BUS/PLU	+2.94	$\log_{\text{sol}} K$
Initial selected value	+2.94	

Using this value, the initial selection for $\Delta_f H^\circ(\text{BaCO}_3, \text{cr}) = -1210.79 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ and with auxiliary information from 89COX/WAG for $\Delta_f H^\circ(\text{CO}_3^{2-}, \text{aq})$, $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao}) = -532.62 \pm 2.2 \text{ kJ}\cdot\text{mol}^{-1}$.

7.1.3. The Standard Enthalpy of Solution of $\text{Ba}(\text{NO}_3)_2(\text{cr})$

Table 6 summarizes the available calorimetric determinations and their ΔH° values. Values for $\phi_L(\text{Ba}(\text{NO}_3)_2)$ were obtained from 82WAG/EVA from the measurements of 31LAN/STR, 37BIR/LAN, 18PRA and 08BIS.

TABLE 6. The $\Delta_{\text{sol}}H^\circ(\text{Ba}(\text{NO}_3)_2, \text{cr})$ in H_2O at 298.15 K; $\text{Ba}(\text{NO}_3)_2(\text{cr}) = \text{Ba}(\text{NO}_3)_2(\text{ai})$

Investigator	$\Delta H(T)$ $\text{kJ}\cdot\text{mol}^{-1}$	$n\text{H}_2\text{O}$	T/K	ϕ_L $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{sol}}H^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$
1875BER2	35.02	1000	285.15 ^a	-0.414	35.44
1886THO	39.35	400	293.8 ^b	-1.61	39.74
1898STA	41.98	1000	289.15 ^c	-0.414	39.68
23TAM/KRI	43.51	200	279.15 ^d	-3.573	40.73
37BRO/SMI	38.685	614	298.15	-1.00	39.68
64VAS	39.66	1000 ^e	298.15	-0.414	40.08
Initial Selection					39.68 ± 0.30

^a $\Delta C_p = -293 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^b $\Delta C_p = -264 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^c $\Delta C_p = -301 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^d $\Delta C_p = -334 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^eassumed.

Using $\Delta H^\circ = 39.68 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ and auxiliary data from 89COX/WAG, our selection for $\Delta_f H^\circ(\text{Ba}(\text{NO}_3)_2(\text{cr})) = -987.25 \pm 1.8 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao}) = -533.88 \pm 1.82 \text{ kJ}\cdot\text{mol}^{-1}$.

7.2. The $S^\circ(\text{Ba}^{2+}, \text{ao})$

The values for $S^\circ(\text{Ba}^{2+}, \text{ao})$ are derived from the $\Delta_{\text{sol}} S^\circ$ from the solution properties of $\text{BaCl}_2\cdot 2\text{H}_2\text{O}(\text{cr})$, $\text{BaCO}_3(\text{cr})$ and $\text{Ba}(\text{NO}_3)_2(\text{cr})$. The entropies used for these compounds and $\text{Ba}(\text{cr})$ and for other compounds of interest in this evaluation are tabulated.

TABLE 7. Accepted Entropies of Solid Phases

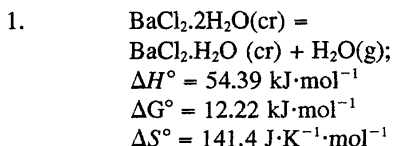
Compound	$S^\circ(298.15 \text{ K}), \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Source
Ba(cr)	62.475 ± 0.8	85CHA/DAV
BaO(cr)	72.069 ± 0.38	85CHA/DAV
BaH ₂ (cr)	63.00 ± 6	81GUR/BER
BaCl ₂ (cr)	123.666 ± 0.13	85CHA/DAV
BaCl ₂ ·2H ₂ O(cr)	202.97 ± 0.84	61KEL/KIN
Ba(NO ₃) ₂ (cr)	213.97 ± 0.84	61KEL/KIN
BaCO ₃ (cr)	112.10 ± 2.0	81GUR/BER

7.2.1. From the Solution Properties of $\text{BaCl}_2\cdot 2\text{H}_2\text{O}(\text{cr})$

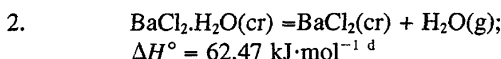
The Enthalpy of Solution and the Enthalpy of Dehydration

Table 8 shows the various calorimetric measurements and the $\Delta_{\text{sol}} H^\circ$ obtained using ϕ_L from 82WAG/EVA.

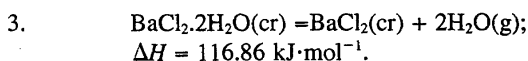
For the enthalpy of dehydration to $\text{BaCl}_2(\text{cr})$:
The vapor pressure measurements of *L. Trip* were reported by 29HUT/SLO. For:



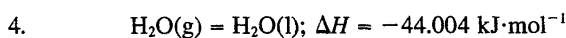
and



so that



Using CODATA Key Values [89COX/WAG] for,



the $\Delta_{\text{dehyd}} H^\circ = 28.8 \text{ kJ}\cdot\text{mol}^{-1}$ for



The measurements of 65RIG/ING by DTA, using a N₂ carrier gas in the range 309K to 355K yield for (1)

$$\begin{aligned} \Delta H^\circ &= 69.83 \pm 3.0 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta G^\circ &= 14.43 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta S^\circ &= 185.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

Measurements in the range 351 K to 386 K for (2) result in

$$\begin{aligned} \Delta H^\circ &= 79.9 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta G^\circ &= 18.8 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta S^\circ &= 205.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

TABLE 8. $\Delta_{\text{sol}} H^\circ(\text{BaCl}_2\cdot 2\text{H}_2\text{O}, \text{cr})$ at 298.15 K

Investigator	ΔH $\text{kJ}\cdot\text{mol}^{-1}$	conc $n \text{ H}_2\text{O}/\text{BaCl}_2$	ϕ_L $\text{kJ}\cdot\text{mol}^{-1}$	ΔH° $\text{kJ}\cdot\text{mol}^{-1}$
1875BER	17.76 ^a	280	2.105	15.66
1886THO	18.63 ^b	400	1.933	16.71
08SCH	18.38 ^c	400	1.933	16.31
65LES/AVE	17.45 ± 0.10	1000	1.523	15.92
36BRO/SMI	18.49	402	1.933	16.56
36SHI/TER	18.27	1000	1.523	16.75
29PER	18.06 ^d	430	1.900	16.16
37FED/SIL	19.12 ^e	400	1.933	17.17
	19.80 ^e	200	2.246	17.55
	20.17 ^e	100	2.500	17.67
73SMI/BER				16.29
Initial Selected Value				16.50 ± 0.50

^aFrom 283 K, $\Delta H = 21.84 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -272 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^bFrom 291 K, $\Delta H = 20.63 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -276 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^cFrom 290 K, $\Delta H = 20.585 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -276 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^dFrom 285 K, $\Delta H = 21.76 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -285 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^eFrom 292 K, $\Delta H = 20.87 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -289 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (400 H₂O).

$\Delta H = 21.28 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -247 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (200 H₂O).

$\Delta H = 21.55 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta C_p = -230 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (100 H₂O).

^d $\Delta H^\circ = 62.22 \text{ kJ}\cdot\text{mol}^{-1}$ at a mean $T = 338 \text{ K}$, $\Delta C_p = -6.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

so that $\Delta H^\circ(5) = 61.73$ kJ. These measurements are rejected. In addition, since many of the investigators measured the $\Delta_{\text{sol}}H$ of both the hydrate and the anhydrous salt, one can obtain $\Delta_{\text{dehyd}}H^\circ$ from $\Delta(\Delta_{\text{sol}}H^\circ)$.

Table 9 shows the values obtained, as well as that from 29HUT/SLO.

TABLE 9. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr}) = \text{BaCl}_2(\text{cr}) + 2\text{H}_2\text{O}(\text{l})$

Investigator	ΔH , $\text{kJ} \cdot \text{mol}^{-1}$
1875BER	29.77
1886THO	29.78
08SCH	29.61
25KOL	31.23
38KHO	27.53
73SMI/BER	29.92
29HUT/SLO	28.6
From initial $\Delta_{\text{sol}}H^\circ$'s	30.30 ± 0.31 .
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr}) = 16.5 \pm 0.30$ $\text{kJ} \cdot \text{mol}^{-1}$ and $\text{BaCl}_2(\text{cr}) = -13.80 \pm 0.10$ $\text{kJ} \cdot \text{mol}^{-1}$.	

The $\Delta_{\text{sol}}G^\circ$ and $\Delta_{\text{sol}}S^\circ(\text{BaCl}_2 \cdot 2\text{H}_2\text{O}, \text{cr})$

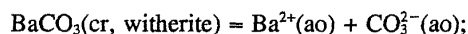
The saturated solution of aqueous BaCl_2 contains 1.785 moles $\text{BaCl}_2/\text{kg H}_2\text{O}$ as given by 58 LIN. 78GOL/NUT evaluate the activity coefficient and osmotic coefficient measurements and recommend γ_{\pm} and a_w to be 0.4417 and 0.9028 respectively. These values result in $\Delta_{\text{sol}}G^\circ = -1.16 \pm 0.20$ $\text{kJ} \cdot \text{mol}^{-1}$ for



Using the initial selection of $\Delta_{\text{sol}}H^\circ = 16.5 \pm 0.30$ $\text{kJ} \cdot \text{mol}^{-1}$, $\Delta_{\text{sol}}S^\circ = 59.23 \pm 1.21$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $S^\circ(\text{Ba}^{2+}, \text{ao}) = 9.10 \pm 1.47$ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

7.2.2. The Solution Properties of $\text{BaCO}_3(\text{cr})$

86BUS/PLU measured the solubility of $\text{BaCO}_3(\text{cr}, \text{witherite})$ from 273.15K to 363.15K at 1 atm. They represent their results for:



$\log K = 607.642 + 0.121098T - 20011.25/T - 236.4948 \log T$ so that

$$\begin{aligned}\log K (298.15\text{K}) &= -8.562 \\ \Delta H^\circ &= 2.94 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta G^\circ &= 48.87 \pm 0.08 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta S^\circ &= -154.0 \pm 3.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.\end{aligned}$$

Then $S^\circ(\text{Ba}^{2+}, \text{ao}) = 8.10 \pm 3.9$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

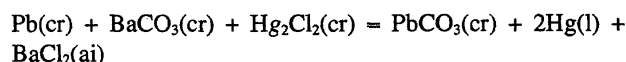
They also review and cite the earlier measurement. Some of those in agreement for ΔG° are:

84MIL/MIL	48.86 $\text{kJ} \cdot \text{mol}^{-1}$
11McC/SMI	48.97 $\text{kJ} \cdot \text{mol}^{-1}$

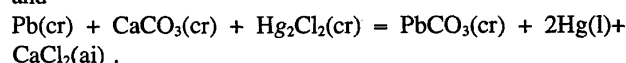
Some others, in fair agreement, are:

39HOG/JOH from (37TOW/WHI) 49.62 $\text{kJ} \cdot \text{mol}^{-1}$ (50.23 $\text{kJ} \cdot \text{mol}^{-1}$) and 60GAR/THO 49.5 $\text{kJ} \cdot \text{mol}^{-1}$.

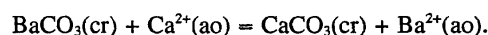
In addition 62JAK/JAN from cell measurements obtained $E^\circ = 0.524$ volts and $E^\circ = 0.532$ volts for respectively for



and



This results in $\Delta G^\circ = 1.54$ $\text{kJ} \cdot \text{mol}^{-1}$ for



Since

$$\begin{aligned}\text{CaCO}_3(\text{cr}) &= \text{Ca}^{2+}(\text{ao}) + \text{CO}_3^{2-}(\text{ao}); \\ \Delta G^\circ &= +48.37 \pm 0.20 \text{ kJ} \cdot \text{mol}^{-1} \text{ from 87GAR/PAR.} \\ \text{BaCO}_3(\text{cr}) &= \text{Ba}^{2+}(\text{ao}) + \text{CO}_3^{2-}(\text{ao}); \\ \Delta G^\circ &= 49.91 \text{ kJ} \cdot \text{mol}^{-1}.\end{aligned}$$

The measurements of 86BUS/PLU are preferred.

7.2.3. The Solution Properties of $\text{Ba}(\text{NO}_3)_2(\text{cr})$

The $\Delta_{\text{sol}}G^\circ = 13.374 \pm 0.20$ $\text{kJ} \cdot \text{mol}^{-1}$ is obtained from the solubility from 58LIN ($m=0.3909$ $\text{mol} \cdot \text{kg}^{-1}$ and $\gamma_{\pm}=0.267$ from 69WU/HAM.

The resultant $\Delta_{\text{sol}}S^\circ$ from $\Delta_{\text{sol}}G^\circ$ and $\Delta_{\text{sol}}H^\circ$ (39.68 ± 0.30 $\text{kJ} \cdot \text{mol}^{-1}$) is 88.23 ± 1.21 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $S^\circ(\text{Ba}^{2+}, \text{ao}) = +8.80 \pm 1.47$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

7.3. Summary of Values Obtained for $S^\circ(\text{Ba}^{2+}, \text{ao})$ and $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao})$

The values obtained for $S^\circ(\text{Ba}^{2+}, \text{ao})$ and $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao})$ are tabulated.

8. The Recommended Thermodynamic Property Values for $\text{Ba}^{2+}(\text{ao})$ and the Key Compounds

Table 10 shows the derived values for $\text{Ba}^{2+}(\text{ao})$ and the selected values. They are:

$$\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao}) = -534.64 \pm 1.8 \text{ kJ} \cdot \text{mol}^{-1};$$

$$S^\circ(\text{Ba}^{2+}, \text{ao}) = 8.80 \pm 0.50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1};$$

$$\Delta_f G^\circ(\text{Ba}^{2+}, \text{ao}, 0.1\text{MPa}) = -557.60 \pm 1.81 \text{ kJ} \cdot \text{mol}^{-1}$$

The derived values in Table 10 for $\Delta_f H^\circ$ and S° from the three systems are in good agreement with each other, lending support to the selections made for the various components. This is particularly true for the $S^\circ(\text{Ba}^{2+}, \text{ao})$, resulting from

three independent paths. For $\Delta_f H^\circ(\text{Ba}^{2+}, \text{ao})$, however, the three values ultimately trace back to the $\Delta_{\text{sol}} H(\text{Ba}, \text{cr})$ in aqueous HCl from 73FIT/HUB. All $\Delta_f H^\circ$'s hang from this. There is no independent path that confirms the $\Delta_f H^\circ$'s for $\text{BaCl}_2(\text{cr})$ and $\text{BaO}(\text{cr})$ and the $\Delta(\Delta_f H^\circ)$. $\Delta_f H^\circ(\text{Ba}(\text{NO}_3)_2, \text{cr})$ and $\Delta_f H^\circ(\text{BaCO}_3, \text{cr})$ are dependent upon them. As is indicated in Sec. 2.1, the direct combustion value for $\Delta_f H^\circ(\text{BaO}, \text{cr})$ is incompatible with 73FIT/HUB's value from $\Delta_{\text{sol}} H(\text{Ba}, \text{cr})$ and $\Delta_{\text{sol}} H(\text{BaO}, \text{cr})$ in aqueous HCl. The 90COR/KON measurements establish the $(\Delta_f H^\circ(\text{BaO}, \text{cr}) - \Delta_f H^\circ(\text{BaCl}_2, \text{cr}))$. The independent measurements of 63EHR/PEI on $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ from $\Delta_{\text{sol}} H^\circ$'s of $\text{Ba}(\text{cr})$ and $\text{BaCl}_2(\text{cr})$ in HCl are farther off from the 90COR/KON to be considered good confirmation. The only other independent path, the di-

rect $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$ from the enthalpy of hydrogenation from 68VOR/MON, which confirms the indirect $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$ from 67VOR/MON (see Chapter 5), is also incompatible with $\Delta_f H^\circ(\text{BaCl}_2, \text{cr})$ (see Chapter 3).

Further work is needed to confirm the above selections. Specifically, the $\Delta_{\text{sol}} H(\text{Ba}, \text{cr})$, $\Delta_{\text{sol}} H(\text{BaO}, \text{cr})$, $\Delta_{\text{sol}} H(\text{BaCl}_2, \text{cr})$ and $\Delta_{\text{sol}} H(\text{BaCO}_3, \text{cr})$ in HCl should be remeasured and the direct $\Delta_f H^\circ(\text{BaH}_2, \text{cr})$ redetermined and the $\Delta_{\text{sol}} H$ of this well-characterized sample measured.

Table 11 shows the final recommended property values for the key compounds.

Table 12 shows the reconstituted recommended process values and their uncertainties for processes considered here.

TABLE 10. The thermodynamics for $\text{Ba}^{2+}(\text{ao})$. The calculated values for $\Delta_f H^\circ$ and S° for $\text{Ba}^{2+}(\text{ao})$ from the processes considered

Process	ΔH° $\text{kJ}\cdot\text{mol}^{-1}$	ΔG° $\text{kJ}\cdot\text{mol}^{-1}$	ΔS° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	S° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$\text{BaCl}_2(\text{cr}) = \text{BaCl}_2(\text{ai})$ and $\Delta_f H^\circ(\text{BaCl}_2, \text{cr}) = -855.00 \pm 1.73 \text{ kJ}\cdot\text{mol}^{-1}$	-13.80 ± 0.10	—	—	-534.64 ± 1.8	
$\text{BaCl}_2\cdot 2\text{H}_2\text{O}(\text{cr}) = \text{BaCl}_2(\text{ai}) + 2\text{H}_2\text{O}(\text{l})$	+16.5 ± 0.30	-1.16 ± 0.20	59.23 ± 1.21		9.10 ± 1.47
$\text{BaCO}_3(\text{cr}) = \text{BaCO}_3(\text{ai})$ and $\Delta_f H^\circ(\text{BaCO}_3, \text{cr}) = -1210.79 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$	2.94 ± 1.0	48.87 ± 0.08	-154.0 ± 3.4	-532.62 ± 2.2	8.10 ± 3.9
$\text{Ba}(\text{NO}_3)_2(\text{cr}) = \text{Ba}(\text{NO}_3)_2(\text{ai})$ and $\Delta_f H^\circ(\text{Ba}(\text{NO}_3)_2, \text{cr}) = -987.25 \pm 1.8 \text{ kJ}\cdot\text{mol}^{-1}$	39.68 ± 0.30	13.37 ± 0.20	88.23 ± 1.21	-533.88 ± 1.82	8.80 ± 1.47
Selected Values				-534.64 ± 1.8	8.80 ± 0.50

TABLE 11. Recommended thermodynamic property values of key compounds of Barium at 298.15 K and 0.1MPa (1 bar)

	$\Delta_f H^\circ(0)$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ$ (298.15 K) $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f G^\circ$ (298.15 K) $\text{kJ}\cdot\text{mol}^{-1}$	$H-H(0)$ $\text{kJ}\cdot\text{mol}^{-1}$	S° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	C_p° $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$\text{Ba}(\text{cr})$	0	0	0	6.912	62.47 ± 0.8	28.096
$\text{Ba}^{2+}(\text{ao})$	—	-534.64 ± 1.8	-557.60 ± 1.81	—	8.80 ± 0.50	—
$\text{BaO}(\text{cr})$	-546.771	-548.04 ± 1.72	-520.32 ± 1.73	9.983	72.069 ± 0.38	47.279
$\text{BaH}_2(\text{cr})$	-170.72	-177.0 ± 4.0	-138.2 ± 4.4	9.10 ± 0.90	63.0 ± 6.0	46.0 ± 2.0
$\text{BaCl}_2(\text{cr})$	-855.614	-855.00 ± 1.73	-806.73 ± 1.73	16.707 ± 0.03	123.666 ± 0.13	75.140 ± 0.13
$\text{BaCl}_2(\text{ai})$	—	-868.80 ± 1.74	-820.04 ± 1.74	—	122.00	—
$\text{BaCl}_2\cdot 2\text{H}_2\text{O}(\text{cr})$	—	-1456.86 ± 1.8	-1293.16	—	202.97 ± 0.84	—
$\text{Ba}(\text{NO}_3)_2(\text{cr})$	—	-988.02 ± 1.8	-792.562	—	213.97 ± 0.84	—
$\text{Ba}(\text{NO}_3)_2(\text{ai})$	—	-948.34	-779.188	—	302.20	—
$\text{BaCO}_3(\text{cr})$	-1208.558	-1213.03 ± 2.0	-1134.37	16.510 ± 0.13	112.10 ± 2.0	85.983 ± 0.6
$\text{BaCO}_3(\text{ai})$	—	-1209.87	-1085.50	-41.20	—	—

TABLE 12. Recommended process values for some Ba compounds at 298.15 K and 0.1 MPa (1 bar)

Reaction	ΔH° kJ·mol ⁻¹	ΔG° kJ·mol ⁻¹	ΔS° J·K ⁻¹ ·mol ⁻¹
1. Ba(cr) + 2H ⁺ (ao) = Ba ²⁺ (ao) + H ₂ (g)	-534.64 ± 1.80	-557.60 ± 1.81	77.01 ± 0.94
2. BaO(cr) + 2H ⁺ (ao) = Ba ²⁺ (ao) + H ₂ O(l)	-272.43 ± 0.28	-274.42 ± 0.34	6.68 ± 0.63
3. BaH ₂ (cr) + 2H ⁺ (ao) = Ba ²⁺ (ao) + 2H ₂ (g)	-357.64 ± 4.0	-419.4 ± 4.5	207.2 ± 6.1
4. BaO(cr) + 2HCl(ai) = BaCl ₂ (cr) + H ₂ O(l)	-258.63 ± 0.30	-261.11 ₄ ± 0.40	8.35 ± 0.57
5. BaCl ₂ (cr) = BaCl ₂ (ai)	-13.80 ± 0.10	-13.31 ± 0.22	-1.67 ± 0.65
6. BaCl ₂ ·2H ₂ O(cr) = BaCl ₂ (ai) + 2H ₂ O(l)	16.40 ± 0.30	-1.16 ± 0.20	58.90 ± 1.1
7. BaCl ₂ (cr) + 2HNO ₃ (ai) = Ba(NO ₃) ₂ (cr) + 2HCl(ai)	167.48 ± 0.50		
8. Ba(NO ₃) ₂ (cr) = Ba(NO ₃) ₂ (ai)	39.68 ± 0.30	13.37 ± 0.20	88.2 ± 1.2
9. BaCO ₃ (cr) = BaO(cr) + CO ₂ (g)	271.48 ± 1.0	219.68 ± 1.2	173.75 ± 2.1
10. BaCO ₃ (cr) = Ba ²⁺ (ao) + CO ₃ ²⁻ (ao)	3.16 ± 0.7	38.87 ± 0.08	-153.30 ± 2.3

9. Closing Comments

Table 12 shows the thermochemical property values for the alkaline earth metal ions on the CODATA scale, including the values presented here for Ba²⁺(ao), those of 86BUS/PLU on Sr²⁺(ao), and the others from the recommendations of 89COX/WAG. It is interesting to note that the values for the $\Delta_f G^\circ$ s for the alkaline earth ions become more negative with increasing atomic number, as is the case for the comparable alkali metal ions^c, except for Ba²⁺(ao) which reverses directions and is more positive than Sr²⁺(ao), in keeping with the trends of other aqueous ions within a group of the periodic chart. An estimate for $\Delta_f G^\circ$ (Ra²⁺,ao) based on this would be $-550 \pm 5 \text{ kJ mol}^{-1}$.

TABLE 13. The alkaline earth metal ions on the CODATA scale at 298.15 K and 0.1 MPa

	$\Delta_f H^\circ$, kJ·mol ⁻¹	$\Delta_f G^\circ$, kJ·mol ⁻¹	S° , J·K ⁻¹ ·mol ⁻¹
Mg ²⁺ (ao)	-467.0 ± 0.6	-455.38 ± 1.4	-137 ± 4
Ca ²⁺ (ao)	-543.0 ± 1.0	-552.81 ± 1.1	-56.2 ± 1.0
Sr ²⁺ (ao)	-550.90 ± 0.5	-563.86 ± 0.8	-31.5 ± 2.0
Ba ²⁺ (ao)	-534.64 ± 1.8	-557.60 ± 1.81	8.80 ± 0.5

^cThe values for $\Delta_f G^\circ$ (M⁺,ao) at 298.15 K and 0.1 MPa are -261.98, -282.53, -284.03, and -291.48 kJ·mol⁻¹ respectively where M = Na, K, Rb, and Cs. These were calculated from the values for $\Delta_f H^\circ$ and S° given by 89COX/WAG and converted to 0.1 MPa.

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Note added in proof:

After the network solution was completed the results of Cordefunke *et al.*, J. Phys. Chem. Solids **55**, 77 (1994) on the S° (BaO,cr) became available. The $S^\circ = 70.01 \pm 0.10 \text{ J·K}^{-1}\text{·mol}^{-1}$ differs from that recommended here by 2.06 J·K⁻¹·mol⁻¹. This would lower all third law $\Delta_{\text{decomp}} H^\circ$ (BaCO₃,cr) from vapor pressure measurements listed in Table 1 by ~2 kJ. It would not appreciably affect the final recommendation within the assigned uncertainties.

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