

THE THERMOCHEMISTRY OF RADIUM

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ABSTRACT

The thermochemistry of radium is reviewed and extended by correlation for a wide range of compounds.

INTRODUCTION

Following the death of Marie Curie in 1934, research on the chemistry of radium fell into a period of neglect and has only recently been revived in the research schools of V.M. Vdovenko in Leningrad and F. Weigel in Munich. The paucity of information is reflected in literature reviews on radium chemistry [1–4]. These texts are rather short or strongly biased towards the commercial methods of recovery, nuclear properties and the preparation of emanating sources. The associated thermochemical data are correspondingly sparse, fitting, for example, onto one page of the National Bureau of Standards Technical Note 270-6 [5]. No heat capacity data are reported for the element or its compounds.

The recognition of the biological hazard of radium/radon associated with the mining and milling of uranium has created a renewed interest in radium chemistry and an accompanying demand for thermodynamic data. Although experimental data are to be preferred, a reasonable picture of the thermochemistry may be built up by a number of techniques. This paper reports on results from these techniques, comparing the values obtained with the few experimental results that are available. All values are reported in S.I. units based on the conversion $1 \text{ cal} = 4.184 \text{ J}$.

TECHNIQUES FOR ESTIMATING THE THERMODYNAMIC PROPERTIES AT 298.15 K (25°C)

Some physical properties of the element are listed in Table 1. Values for the enthalpy of formation, ΔH_f , the Gibbs free energy of formation, ΔG_f ,

TABLE 1
Physical properties of radium

Property	Value	Reference
Density	ca. 6 g cm ⁻³	22,23
Melting point	ca. 700°C	23,24
	ca. 960°C	23,25
Boiling point	ca. 1140°C	23,25
Ionic radius	0.152 nm	23,26
	0.137 nm	23,27
Crystal radius	0.235 nm	23,27
Ionization potential		
first electron	5.26 eV	23,28
second electron	10.10 eV	23,28
Standard reduction potential		
Ra(II) + 2e → Ra	-2.92 V (SHE)	23,29

the entropy, S , and the heat capacity at constant pressure, C_p , for radium and some of its compounds in their standard state and at 298.15 K are listed in Table 2. Experimental values are given in Roman type and estimated values in italics. Similarly, all compounds which have been prepared are given in Roman type even if there are no reported experimentally measured values for the thermodynamic constants of these compounds. Compounds which have not been prepared are in italics.

The experimental thermodynamic data for radium and its compounds have been taken completely from the National Bureau of Standards Technical Note 270-6 [5]. The experimental data for the correlations have been taken in the main from the same source but incorporate the corrections given in the National Bureau of Standards Technical Note 270-8 [5]. Other sources of experimental data are cited in this report.

The estimated values are divided into two groups: one group contains estimates reported in the literature, in which case the data are referenced in the text; the other are estimates determined by the author, in which case the method of estimation is denoted by a mnemonic, as discussed below.

EM

Eberhart and McDonald [6] discussed a number of methods for correlating thermodynamic data. The most useful of these was a plot of ΔH_f against ΔG_f which in many cases yielded a straight line, and, provided that either ΔH_f or ΔG_f was known for the radium compound, allowed the other property to be estimated with reasonable certainty. The method could not be applied to S and C_p but other methods were available to determine these properties. In some cases, the ΔH_f value passed through a maximum with increasing atomic number across the alkaline-earth series; a reasonable

TABLE 2
Thermodynamic properties of radium and of some of its compounds at 298.15 K (25°C)

Substance	formula and description	State	Formula weight	ΔH_f (kJ mol ⁻¹)	ΔG_f (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)	C_p (J K ⁻¹ mol ⁻¹)
Ra		c	226.05	0	0	71.1	20.8
Ra ⁺		g		159.0	129.7	176.4	
Ra ²⁺		g		674.5			
		g		1659.8			
	std. state, $m = 1$	aq		-527.6	-561.5	54.4	
RaO		c	242.02	-523.0	-511.0	76.2	46.4
RaO ₂		c	258.24	-598.0	-704.0	3.7	64.0
Ra(OH) ⁺		aq	243.05	-757.0	-728.0	46.4	
Ra(OH) ₂ un-ionised		aq	260.04	-987.0	-895.0	38.3	
Ra(OH) ₂ neut. elect.		aq	260.04	-988.0	-876.0	32.9	
Ra(OH) ₂		c	260.04	-950.0	-838.0	117.0	89.2
RaH		g	227.08	-223.0	-195.0	227.0	30.3
RaH ₂		c	228.11	-151.0	-142.0	78.4	44.8
RaF		g	245.04	-348.0	-372.0	234.0	50.0
RaF ₂		c	264.02	-1201.0	-1197.0	100.0	73.6
RaCl		g	261.49	-208.0	-233.0	-265.0	38.0
RaCl ₂		c	296.93	-887.0	-841.0	134.0	76.5
	std. state, $m = 1$	aq		-861.9	-823.8	167.4	
RaCl ₂ ·1H ₂ O		c	332.96	-1464.4	-1302.9	213.4	163.0
Ra(ClO ₃) ₂		c	392.93	-87.0	-620.0	180.0	167.0
Ra(ClO ₄) ₂		c	424.93	-845.0	-527.0	190.0	172.0
Ra(ClO ₄) ₂		aq		-810.0	-580.0	418.0	
RaBr ₂		c	385.83	-770.0	-720.0	153.0	81.0
RaBr ₂		g		-448.0	-502.0	339.0	62.0
	std. state, $m = 1$	aq		-770.0	-770.0	213.0	
RaBr ₂ ·2H ₂ O		c	421.86	-1385.0	-1238.0	224.0	171.0
Ra(BrO ₃) ₂		c	481.80	-711.0	-611.0	256.0	172.0
Ra(BrO ₃) ₂ ·H ₂ O		c	499.80	-1013.0	-858.0	302.0	217.0

TABLE 2 (continued)

Substance formula and description	State	Formula weight	ΔH_f (kJ mol ⁻¹)	ΔG_f (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)	C_p (J K ⁻¹ mol ⁻¹)
RaI ₂	c	479.83	-640.0	-594.0	176.0	84.0
RaI ₂	g		-377.0	-418.0	351.0	63.0
std. state, <i>m</i> = 1	aq		-640.0	-665.0	271.0	
RaI ₂ ·0.5H ₂ O	c	488.84	-796.0	-724.0	199.0	106.0
Ra(IO ₃) ₂	c	575.83	-1027.0	-869.0	272.0	188.0
std. state, <i>m</i> = 1	aq		-979.0	-820.0	268.0	
Ra(IO ₃) ₂ ·H ₂ O	c	588.86	-1320.0	-1102.0	307.0	234.0
RaS	c	258.09	-446.0	-423.0	85.0	52.0
Ra(HS)	c	292.16	-548.0			
RaSO ₃	c	306.08	-1180.0	-1089.0	133.0	96.0
RaSO ₄	c	322.09	-1471.0	-1366.0	138.0	103.0
std. state, <i>m</i> = 1	aq		-1437.0	-1306.0	75.0	
Ra(HSO ₄) ₂	c	420.16	-2326.0			
RaSe	c	304.96	-360.0	-350.0	92.0	53.0
RaSeO ₃	c	352.96	-1033.0	-970.0	174.0	100.0
RaSeO ₄	c	368.96	-1175.0	-1050.0	180.0	108.0
RaTe	c	353.6				54.0
RaPo	c	434.00				54.0
Ra(N ₃) ₂	c	310.04	-4.0	-170.0	170.0	
Ra ₃ N ₂	c	706.01	-335.0			
Ra(NH ₂) ₂	c	258.05	-330.0			
Ra(NO ₂) ₂	c	318.00	-774.0			
Ra(NO ₃) ₂	c	350.03	-992.0	-796.0	222.0	154.0
std. state, <i>m</i> = 1	aq		-942.0	-784.0	347.0	
Ra ₃ (PO ₄) ₂	c	867.94	-4170.0	-3974.0		
RaC ₂	c	250.02	-80.0			
RaCO ₃	c	286.03	-1222.0	-1142.0	123.0	85.0
Ra(HCO ₃) ₂	c	348.03	-1979.0			
RaC ₂ O ₄ (oxalate)	c	314.02	-1410.0			

<i>Ra</i> (<i>CHO</i> ₂) ₂ (formate)	c	284.04	- 1376.0			
<i>Ra</i> (<i>CH</i> ₃ <i>CO</i> ₂) ₂ (acetate)	c	344.09	- 1498.0			
<i>Ra</i> (<i>CN</i>) ₂ (cyanide)	c	278.04	- 217.0			
<i>RaCN</i> ₂ (cyanamide)	c	266.02	- 234.0			
<i>Ra</i> (<i>CNS</i>) ₂	c	342.16	- 406.0			
<i>RaSiO</i> ₃ (metasilicate)	c	302.08	- 1577.0	120.0	91.0	
<i>Ra</i> ₂ <i>SiO</i> ₄ (orthosilicate)	c	544.08	- 2268.0	195.0	136.0	
<i>Ra</i> (<i>ReO</i> ₄) ₂	c	726.39	- 2167.0			
<i>RaCrO</i> ₄	c	342.00	- 1440.0	160.0	118.0	
<i>RaMoO</i> ₄	c	385.94	- 1570.0	157.0	118.0	
<i>RaWO</i> ₄	c	473.85	- 1693.0	166.0	125.0	
<i>RaY</i> ₂ <i>O</i> ₆	c	423.88		253.0	184.0	
<i>Ra</i> ₂ <i>Y</i> ₂ <i>O</i> ₇	c	665.88		290.0	226.0	
<i>RaTiO</i> ₃	c	321.90	- 1640.0	123.0	103.0	
<i>Ra</i> ₂ <i>TiO</i> ₄	c	563.90	- 2197.0	214.0	160.0	
<i>RaZrO</i> ₃	c	365.22	- 1785.0	143.0	105.0	
<i>RaCeO</i> ₃	c	414.12				
<i>RaBeF</i> ₄	c	311.01				

estimate could then be made simply by inspecting the trend within the group.

Hr

Where possible, Kubaschewski and Unal's equation [7] was used to determine C_p (see below, under *KU*). However, for lack of suitable data, the equation of Herz [8,9] was used

$$S = 5nC_p^{-1/3}$$

where n is the number of atoms in the molecule. Test calculations with compounds with known C_p values indicated that results from this equation should be treated with caution.

Hy

Examination of the thermodynamic properties of the hydrates of alkaline-earth salts revealed that their properties are additive with respect to the number of water molecules in the compound, so for a property Z

$$Z(\text{MX} \cdot n\text{H}_2\text{O}) = Z(\text{MX}) + nZ(\text{Av} \cdot \text{H}_2\text{O})$$

where MX is the salt. The value for the second term on the right-hand side (RHS) varied marginally with the anion X , and the number of hydrating water molecules n . However, provided that sufficient data were available from other members of the alkaline-earth series, a reasonable estimate could be obtained for the thermodynamic properties of the equivalent hydrated radium salt.

Ka

Kapustinskii [10] developed a rule of thermochemical logarithmicity for ΔH_f . He demonstrated that a linear plot was obtained for ΔH_f versus \log (atomic number) for the alkaline and alkaline-earth oxides and halides. Provided that a sufficient amount of data is available, reasonable estimates may be obtained for the corresponding radium compound.

KU

Kubaschewski and Unal [7] developed a method for the empirical estimation of the heat capacity of a compound. The method was based on Kellogg's approach [11], which showed that each component of a compound contributes a characteristic amount Ξ to the heat capacity of the compound. Kubaschewski and Unal were able to simplify the method, so Ξ for each

component was not only independent of the other species but also independent of valency. Thus, the heat capacity is given by

$$C_p(298.15 \text{ K}) = \Sigma \Xi$$

The $KU \Xi$ values did not include a value for radium. An inspection of the Ξ values for the other alkaline-earths allowed an estimate of 2.75 J K^{-1} to be assigned to radium. This value, together with the values listed by Kubaschewski and Unal for the anions, was then used to estimate C_p . Comparison with the measured heat capacities of the alkaline-earth compounds indicated that the estimates were in general agreement with the observed trends through the alkaline-earth group.

NBS

Refers to data taken from the National Bureau of Standards Technical Note 270-6 [5].

Ry

Ryabukhin [12–14] investigated some empirical correlations between metal ions in aqueous solution and the corresponding crystalline hydroxide, for both ΔH_f and ΔG_f . The resulting equations were used to calculate the thermodynamic properties of radium hydroxide.

Ta

Tardy et al. [15–18] reported a set of correlations between the thermodynamic properties of the aqueous ion and metal oxide, hydroxide, silicate, sulphate, nitrate, phosphate and carbonate. The correlations were empirical but allowed reasonable estimates for unmeasured values. The alkaline-earth group deviated most from the general relationship. Accordingly, the parameters for the equations were recalculated using only the data of the alkaline-earth group. This produced excellent correlations and allowed reasonable estimates to be made for the thermodynamic parameters of radium silicate, phosphate and carbonate.

TM

In a review of 20 equations for estimating the entropy of compounds, Khriplovich and Paukov [19,20] found the most reliable one to be that of Treadwell and Mauderli [21]

$$S = a(\log M_c + a \log M_a) + b$$

where M_c and M_a are the molecular weights of the cation and anion,

respectively, a and b are empirical constants to be determined by least-squares analysis and $\alpha = 1$ for 1-1 salts and 2 for 2-1 salts. It could be applied to the widest range of compounds regardless of the crystal structure and ionic composition. The equation was very easy to use and was remarkably linear within such groups as the alkaline-earth oxides.

ESTIMATIONS FOR THE THERMODYNAMIC PROPERTIES OF RADIUM COMPOUNDS

Ra

The preparation of radium metal was discussed in detail by Weigel [4]. Physical properties of the element accrued by a number of authors [22-29] are collated in Table 1. The metal is highly reactive and oxidises immediately on exposure to air. The thermodynamic properties for Ra(c), Ra⁺(g), Ra²⁺(g) and Ra²⁺(aq) listed in Table 2 were obtained from the NBS Technical Note 270-6 [5].

RaO

RaO is a highly aggressive substance which readily attacks crucible and calorimeter materials and no definitive material has been identified to which the formula RaO may be assigned [4]. This accounts for the lack of experimental measurements of the thermodynamic properties.

Values reported for $\Delta H_f(\text{RaO})$, are -523.0 [5], -527.1 [30,31], and -543.9 kJ mol⁻¹ [32,33]. The NBS value was selected for Table 2.

Values reported for $\Delta G_f(\text{RaO})$ are -514.6 [32,33], -491.6 [35] from an unreferenced source, -491.6 [29], -493 estimated from a corrected version of equation 11 of Glassner [34] and using the NBS value for ΔH_f , -573.2 kJ mol⁻¹ estimated using parameters quoted by Wilcox [30]. The value given in Table 2 is an average of the first four estimates.

Although there are no experimentally measured values for $S(\text{RaO})$, the following estimates have been reported: 71 [34], and 76.2 J K⁻¹ mol⁻¹ [TM]. The TM value is used in Table 2.

There is no experimentally measured value for $C_p(\text{RaO})$, but the following estimates have been reported: 46.4 [34], 45.6 [36], and 45.6 J K⁻¹ mol⁻¹ [KU]. The estimate from Glassner [34] was selected for Table 2.

RaO₂

RaO₂ has never been prepared [4]. The following estimates have been reported for $\Delta H_f(\text{RaO}_2)$, -598 [30,31], -627.6 kJ mol⁻¹ [Ka]. The value obtained by Wilcox [30,31] was selected for Table 2 because it is in better

agreement with the general trend for the heats of formation of the alkaline-earth peroxides.

The estimate for $\Delta G_f(RaO_2)$ was -704 kJ mol^{-1} [Ta]. This value should be treated with caution since Tardy and Garrels [15] developed their equations for simple oxides based on a theoretical O^{2-} species. They did not test the applicability of the equation to peroxides.

There are no reported experimental or estimated values for S or C_p for any of the alkaline-earth peroxides, making their estimation by correlation impossible. The estimate for $C_p(RaO_2)$ was $64 \text{ J K}^{-1} \text{ mol}^{-1}$ [KU]. Since the KU method has not been applied to peroxides, it was assumed that the O_2^{2-} contribution was twice that for O^{2-} , which probably underestimates the O_2^{2-} contribution. The estimate for $S(RaO_2)$ was $3.75 \text{ J K}^{-1} \text{ mol}^{-1}$ [Hr]; this value should be treated with caution, since, as a general rule for simple molecules, the value for S is equal to or slightly greater than the value for C_p . On the basis of general trends, the value for S should be about $70 \text{ J K}^{-1} \text{ mol}^{-1}$.

$Ra(OH)_n$

There are no reported experimental or estimated values for any of the thermodynamic constants for the formation of the first or second hydrolysis product of radium. Estimates were made using Lowson's correlations for hydrolysed species [37]. The correlation has the general form

$$Z[M_m(OH)_n^{(mz-n)+}] - Z(M^{z+}) = \delta_z$$

where Z is a thermodynamic property, m and n are stoichiometric coefficients, z is the valency of the free metal and δ_z is a constant for the thermodynamic property Z with the following values: δ_z for $\Delta H_f = -230 \text{ kJ mol}^{-1}$; $\Delta G_f = -167 \text{ kJ mol}^{-1}$; $S = -8 \text{ J K}^{-1} \text{ mol}^{-1}$. These values were used to determine the thermodynamic properties of the hydrolysed products of radium (Table 2).

$Ra(OH)_2(aq)$

For completion, the values for $Ra(OH)_2(aq)$ were calculated with the assumption that the properties were those of a neutral electrolyte; that is, the values are the algebraic sum of the properties of the individual ions which make up the electrolyte using the following values for the OH^- ion: $\Delta H_f = -230 \text{ kJ mol}^{-1}$; $\Delta G_f = 157 \text{ kJ mol}^{-1}$; and $S = -11 \text{ J K}^{-1} \text{ mol}^{-1}$.

$Ra(OH)_2(c)$

There are no reports on the preparation of the crystalline hydroxide $Ra(OH)_2(c)$. The following estimates have been reported for $\Delta H_f(Ra-$

$(OH)_2(c)$, -950 [30,31] and -963 kJ mol⁻¹ [Ry]. Wilcox's value [30,31] was selected as it has a better fit with the general trend for the enthalpies of formation of the other crystalline alkaline-earth hydroxides. The following estimates have been reported for $\Delta G_f(Ra(OH)_2(c))$, -895 [Ta] and -819 kJ mol⁻¹ [Ry]. The Wilcox value was again chosen because it was supported by a greater range of data. The following estimates were obtained for $S(Ra(OH)_2(c))$, 117 J K⁻¹ mol⁻¹ [TM], and for $C_p(Ra(OH)_2(c))$, 98 J K⁻¹ mol⁻¹ [KU].

RaH

There are no reports on the preparation of the mono- or di-hydride of radium even though a fairly comprehensive set of thermodynamic properties has been reported for the monohydrides of other members of the alkaline-earth group. Reported values of ΔH_f for the monohydrides of Ca, Sr and Ba are remarkably similar with no trend with changing cation. An estimate of 223 kJ mol⁻¹ for $\Delta H_f(RaH)$ was derived by averaging the values for these three cations. As there is also no trend for the ΔG_f values in this series, $\Delta G_f(RaH)$ was estimated as 195 kJ mol⁻¹ on the same basis.

The estimate for $S(RaH)$ was 227 J K⁻¹ mol⁻¹ [TM] and for $C_p(RaH)$, it was either 30 , based on the slight increase of C_p within the series or 36 J K⁻¹ mol⁻¹ [KU]. The first of these was selected for Table 2.

RaH₂

Data for the alkaline-earth dihydrides are much more limited, but the following estimates have been reported or were calculated: $\Delta H_f(RaH_2)$, -151 kJ mol⁻¹ [30,31] and $\Delta G_f(RaH_2)$, 142 kJ mol⁻¹ [30,31]. Compared with the values for other members of the group, these estimates are low by about 16 kJ mol⁻¹. The estimate for $S(RaH_2)$ was 78 J K⁻¹ mol⁻¹ [TM] based on limited data, and for $C_p(RaH_2)$ it was 45 J K⁻¹ mol⁻¹ [KU].

RaF

There are no reports on the experimental preparation of radium monofluoride. Values for ΔH_f , ΔG_f , S and C_p have been reported for the other alkaline-earth monofluorides, so the following estimates were possible: $\Delta H_f(RaF)$, -348 kJ mol⁻¹ [Ka]; $\Delta G_f(RaF)$, -372 kJ mol⁻¹ [EB]; $S(RaF)$, 254 J K⁻¹ mol⁻¹ [TM]; and $C_p(RaF)$, 50 J K⁻¹ mol⁻¹ [KU]. The estimate for $C_p(RaF)$ appeared to be rather higher than for other compounds in the series. Linear correlations were sought for C_p versus N , the atomic number, $\log(N)$ and $\log(\text{Mol. Wt.})$, but all the correlations were curved. A value of 35 J K⁻¹ mol⁻¹ was estimated from the trend of C_p for the series.

RaF₂

There are a number of reports on the experimental preparation of radium difluoride, its crystal properties have been determined [4], but no thermodynamic properties have been reported for this compound. However, there is a complete set of data for the thermodynamic properties of the other alkaline-earth difluorides, so the corresponding properties for RaF₂ could be estimated by correlation. The following estimates have been reported for $\Delta H_f(\text{RaF}_2)$: -1201 [4,32–34], -1222 [30,31] and -1128 kJ mol⁻¹ [38]. The Brewer estimate [32,33] was selected on the grounds that it was in better agreement with the general trend observed for the ΔH_f values of the other alkaline-earth difluorides.

The following estimates have been reported for $\Delta G_f(\text{RaF}_2)$: -1149 [32–34] and -1197 kJ mol⁻¹ [30]. The Brewer estimate [32,33] was again selected on the grounds that it was in better agreement with the general trend observed for G_f values of the other alkaline-earth difluorides.

Estimates reported or calculated for $S(\text{RaF}_2)$ are 100 [34] and 99 J K⁻¹ mol⁻¹ [TM]. The value calculated by the TM method was selected.

The following estimates have been reported for $C_p(\text{RaF}_2)$: 76 [32,33] and 74 J K⁻¹ mol⁻¹ [36]. Krestov's value [36] was selected on the grounds that it was in better agreement with the general trend observed for the C_p value of the other alkaline-earth difluorides.

RaCl

There are no reports on the experimental preparation of radium monochloride. Values reported for ΔH_f , ΔG_f , S and C_p for the other alkaline-earth monochlorides have allowed the following estimates for the thermodynamic parameters of RaCl to be made by correlation: $\Delta H_f(\text{RaCl})$, -209 kJ mol⁻¹ [Ka]; $\Delta G_f(\text{RaCl})$, -233 kJ mol⁻¹ [EB]; and $S(\text{RaCl})$, 265 J K⁻¹ mol⁻¹ [TM].

An estimate for $C_p(\text{RaCl})$ of 52 J K⁻¹ mol⁻¹ [KU] was rather higher than those for other compounds in the series. Linear correlations were sought for C_p versus N , $\log(N)$ and $\log(\text{Mol. Wt.})$, but all the correlations were curved. A value of 38 J K⁻¹ mol⁻¹ was selected on the basis of the trend of C_p values for the series.

RaCl₂

Although anhydrous RaCl₂ is a well-identified compound [4], with the exception of a value for the entropy, its thermodynamic data have not been reported, although data are available for this material as a dihydrate and in the aqueous state.

The following estimates have been reported for $\Delta H_f(\text{RaCl}_2)$: -870 [30,31], -887 [32–34] and -962 kJ mol⁻¹ [Ka]. The value reported by

Brewer [32,33] was selected on the grounds that it was in better agreement with the general trend observed for the ΔH_f values of the other alkaline-earth dichlorides.

The following estimates have been reported for $\Delta G_f(\text{RaCl}_2)$: -795 [30] and -841 kJ mol^{-1} [32–34]. The Brewer value [32,33] was again selected.

The experimental value for $S(\text{RaCl}_2)$ is $134 \text{ J K}^{-1} \text{ mol}^{-1}$ [NBS]. This is slightly higher than the *TM* estimate of $130 \text{ J K}^{-1} \text{ mol}^{-1}$ and lower than the estimate of $144 \text{ J K}^{-1} \text{ mol}^{-1}$ reported by Brewer [32,33] and Glassner [34]. The experimental value was selected.

The following estimates have been reported for $C_p(\text{RaCl}_2)$: 79 [36], 77 [KU] and $80 \text{ J K}^{-1} \text{ mol}^{-1}$ [32,34]. The *KU* estimate was selected because it was in better agreement with the general trend of C_p for the alkaline-earth dihalides with atomic number.

$\text{RaCl}_2(\text{aq})$, *standard state*, $m = 1$

Experimental values ΔH_f , ΔG_f and S for $\text{RaCl}_2(\text{aq})$, standard state, $m = 1$, listed in Table 2 are taken from the NBS listing. The experimental values correlate well with the values for the other alkaline-earth dichlorides in this state. There are no values for C_p . Empirical equations relating density and specific heat to atomic number have been derived by Karapet'yants et al. [39–41] for the alkaline dichlorides in solution.

$\text{RaCl}_2 \cdot 2\text{H}_2\text{O}$

Experimental values ΔH_f , ΔG_f and S for $\text{RaCl}_2 \cdot 2\text{H}_2\text{O}$ listed in Table 2 are taken from the NBS listing. The experimental values correlate well with the values for the other alkaline-earth dichlorides in this state. $C_p(\text{RaCl}_2 \cdot 2\text{H}_2\text{O})$ was estimated to be $163 \text{ J K}^{-1} \text{ mol}^{-1}$ on account of the very slight trend of C_p for the alkaline-earth dihalides in this state with atomic number.

$\text{Ra}(\text{ClO}_3)_2$

The alkaline-earths form hypochlorites (ClO) chlorites (ClO_2) chlorates (ClO_3) and perchlorates (ClO_4). No oxychloride of radium has been prepared as the pure compound, but there have been studies on the co-crystallization of Ba–Ra chlorates [42,43].

Thermodynamic data for the hypochlorites and chlorites of the alkaline-earths are sparse and usually restricted to ΔH_f values, hence, no correlations were possible for these compounds.

The following estimates have been reported or calculated for radium chlorate: $\Delta H_f(\text{Ra}(\text{ClO}_3)_2)$, -787 kJ mol^{-1} [31]; $\Delta G_f(\text{Ra}(\text{ClO}_3)_2)$, -620 kJ mol^{-1} based on the observation that the ΔG_f value is usually about 170 kJ

mol^{-1} less than the ΔH_f value for salts of oxyanions; $S(\text{Ra}(\text{ClO}_3)_2)$, $54 \text{ J K}^{-1} \text{ mol}^{-1}$ [Hr], which is lower than the estimate for $C_p(\text{Ra}(\text{ClO}_3)_2)$; an estimate of $180 \text{ J K}^{-1} \text{ mol}^{-1}$ is preferred.

An estimate of $167 \text{ J K}^{-1} \text{ mol}^{-1}$ for $C_p(\text{Ra}(\text{ClO}_3)_2)$ was based on the trend for C_p between alkaline and alkaline-earth chlorites listed by Krestov [36]. This estimate is in agreement with the trend in C_p values for the corresponding bromite and iodite compounds of radium.

$\text{Ra}(\text{ClO}_4)_2(c)$

The following estimates have been reported or were calculated for the thermodynamic properties of crystalline radium perchlorate: $\Delta H_f(\text{Ra}(\text{ClO}_4)_2(c))$, -845 kJ mol^{-1} [30]; $\Delta G_f(\text{Ra}(\text{ClO}_4)_2(c))$, -527 kJ mol^{-1} [30]; $S(\text{Ra}(\text{ClO}_4)_2(c))$, $67 \text{ J K}^{-1} \text{ mol}^{-1}$ [Hr], which appears to be lower than the estimate for $C_p(\text{Ra}(\text{ClO}_4)_2(c))$ and an estimate of $190 \text{ J K}^{-1} \text{ mol}^{-1}$ is preferred; $C_p(\text{Ra}(\text{ClO}_4)_2(c))$, $172 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend C_p values for chlorates listed by Krestov [36].

$\text{Ra}(\text{ClO}_4)_2(aq)$

Experimental values have been collated for ΔH_f , ΔG_f and S of the perchlorates of Mg, Ca and Sr in the standard aqueous state [5]. For a given anion, the ΔH_f and ΔG_f values for alkaline-earth compounds in this state tend to a limiting value with increasing atomic number of the cation, from which the following estimates have been made: $\Delta H_f(\text{Ra}(\text{ClO}_4)_2(aq))$, -810 kJ mol^{-1} ; $\Delta G_f(\text{Ra}(\text{ClO}_4)_2(aq))$, -580 kJ mol^{-1} .

Collation of the entropies for the chlorides, sulphates, nitrates and perchlorates of the alkaline-earth compounds in the aqueous standard state revealed a common difference for a given cation pair from which an estimate of $418 \text{ J K}^{-1} \text{ mol}^{-1}$ was made for $S(\text{Ra}(\text{ClO}_4)_2(aq))$.

RaBr_2

There are no reports for the experimental preparation of radium monobromide and experimental values have not been reported for the thermodynamic properties of the monobromides of the other alkaline-earths.

Radium dibromide has been studied by a number of workers [4] but there are no reported experimental values for the thermodynamic properties of this compound. The following estimates for the thermodynamic properties of radium dibromide have been reported: $\Delta H_f(\text{RaBr}_2)$, -770 kJ mol^{-1} [30,31]; $\Delta G_f(\text{RaBr}_2)$, -720 kJ mol^{-1} [30]; $S(\text{RaBr}_2)$, $153 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(\text{RaBr}_2)$, $81 \text{ J K}^{-1} \text{ mol}^{-1}$ [Kr].

RaBr₂(g)

No experimental values have been reported for the thermodynamic properties of gaseous radium dibromide. Values are available for ΔH_f , ΔG_f and S of some of the other alkaline-earth dibromides in the gaseous state [*NBS*] allowed the following estimates to be made for the thermodynamic properties of gaseous radium dibromide: $\Delta H_f(\text{RaBr}_2(\text{g}))$, -448 kJ mol^{-1} [*Ka*]; $\Delta G_f(\text{RaBr}_2(\text{g}))$, -502 kJ mol^{-1} [*Ka*]; $S(\text{RaBr}_2(\text{g}))$, $339 \text{ J K}^{-1} \text{ mol}^{-1}$ [*TM*]; $C_p(\text{RaBr}_2(\text{g}))$, $62 \text{ J K}^{-1} \text{ mol}^{-1}$ using the trend of C_p with molecular weight for $\text{SrBr}_2(\text{g})$ and $\text{BaBr}_2(\text{g})$.

RaBr₂(aq)

No experimental values have been reported for the thermodynamic properties of RaBr_2 in solution. Values for the thermodynamic properties of the remaining alkaline-earth dibromides in aqueous solution [*NBS*], have allowed the following estimates for the thermodynamic properties of radium dibromide in aqueous solution: $\Delta H_f(\text{RaBr}_2(\text{aq}))$, -770 kJ mol^{-1} [*Ka*]; $\Delta G_f(\text{RaBr}_2(\text{aq}))$, -770 kJ mol^{-1} [*Ka*]; $S(\text{RaBr}_2(\text{aq}))$, $213 \text{ J K}^{-1} \text{ mol}^{-1}$ [*TM*].

RaBr₂ · 2H₂O

Two hydrates of radium dibromide have been prepared, $\text{RaBr}_2 \cdot 0.5\text{H}_2\text{O}$ and $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$, but the thermodynamic properties have not been measured for either compound. The thermodynamic properties listed in Table 2 for the dihydrate were determined using the additivity rule for hydrates and the following average increases for the addition of one molecule of water to an alkaline-earth bromide: $\Delta[\Delta H_f] = -308 \text{ kJ mol}^{-1}$; $\Delta[\Delta G_f] = -259 \text{ kJ mol}^{-1}$; $\Delta[S] = 45 \text{ J K}^{-1} \text{ mol}^{-1}$; and $\Delta[C_p] = 45 \text{ J K}^{-1} \text{ mol}^{-1}$.

Ra(BrO₃)₂

There is no report for the preparation of radium bromate. The thermodynamic data for the bromates of the other alkaline-earths are incomplete, although data for some hydrates of these salts have allowed values for the thermodynamic properties of the barium and strontium bromates to be obtained by using the additivity rule for hydrates. The following estimates are for radium bromate: $\Delta H_f(\text{Ra}(\text{BrO}_3)_2)$, -711 kJ mol^{-1} by extrapolation; $\Delta G_f(\text{Ra}(\text{BrO}_3)_2)$, -611 kJ mol^{-1} by extrapolation; $S(\text{Ra}(\text{BrO}_3)_2)$, $256 \text{ J K}^{-1} \text{ mol}^{-1}$ [*TM*], and $C_p(\text{Ra}(\text{BrO}_3)_2)$, $172 \text{ J K}^{-1} \text{ mol}^{-1}$ [36].

Ra(BrO₃)₂H₂O

There are no reports on the preparation of radium bromate mono-hydrate. However, the alkaline-earth bromates form increasingly stable hydrates with

increasing atomic number of the cation and a stable hydrate of radium bromate is to be expected. These hydrates obey the additivity rule of hydrates and the following average increases were found for the addition of one molecule of water to an alkaline-earth bromate: $\Delta[\Delta H_f] = -302 \text{ kJ mol}^{-1}$; $\Delta[\Delta G_f] = -247 \text{ kJ mol}^{-1}$; $\Delta[S] = 46 \text{ J K}^{-1} \text{ mol}^{-1}$; and $\Delta[C_p] = 45 \text{ J K}^{-1} \text{ mol}^{-1}$. These values may be used to determine the thermodynamic properties of any hydrate of radium bromate.

RaI₂

There are no reports on the experimental preparation of radium monoiodide, nor experimental values for the thermodynamic properties of the monoiodides of the other alkaline-earths.

Radium diiodide has been studied by a number of workers [4] but there are no reported experimental values for the thermodynamic properties of this compound. The following estimates have been reported for the thermodynamic properties of radium diiodide: $\Delta H_f(\text{RaI}_2)$, -640 kJ mol^{-1} [30,31]; $\Delta G_f(\text{RaI}_2)$, -594 kJ mol^{-1} [30]; $S(\text{RaI}_2)$, $176 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM] using the entropy data of Khriplovich and Paukov [20] for the alkaline-earth diiodides; $C_p(\text{RaI}_2)$, $84 \text{ J K}^{-1} \text{ mol}^{-1}$ [36].

RaI₂(g)

No experimental values have been reported for the thermodynamic properties of RaI₂(g). Values for ΔH_f , ΔG_f and S of some of the other alkaline-earth diiodides in the gaseous state have allowed the following estimates to be made for the thermodynamic properties: $\Delta H_f(\text{RaI}(g))$, -377 kJ mol^{-1} [Ka]; $\Delta G_f(\text{RaI}_2(g))$, -418 kJ mol^{-1} ; $S(\text{RaI}_2(g))$, $351 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{RaI}_2(g))$, $63 \text{ J K}^{-1} \text{ mol}^{-1}$ which were based on the observed trend.

RaI₂(aq)

No experimental values have been reported for the thermodynamic properties of RaI₂ in solution. Values for the thermodynamic properties of the diiodides of the other alkaline-earths in solution have allowed estimates to be made for the thermodynamic properties: $\Delta H_f(\text{RaI}_2(aq))$, -640 kJ mol^{-1} , based on the observed trend; $\Delta G_f(\text{RaI}_2(aq))$, -665 kJ mol^{-1} , based on the observed trend; $S(\text{RaI}_2(aq))$, $271 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM].

RaI₂ · 0.5H₂O

The hydrate of RaI₂ · 0.5H₂O has been prepared [4], but the thermodynamic properties have not been measured. The values for the thermodynamic properties listed in Table 2 for this compound were estimated using the

additivity rule for hydrates and the following average increases for the addition of one molecule of water to an alkaline-earth iodide: $\Delta[\Delta H_f] = -311 \text{ kJ mol}^{-1}$; $\Delta[\Delta G_f] = -259 \text{ kJ mol}^{-1}$; $\Delta[S] = 37 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta[C_p] = 45 \text{ J K}^{-1} \text{ mol}^{-1}$.

$\text{Ra}(\text{IO}_3)_2$

The preparation of $\text{Ra}(\text{IO}_3)_2$ is discussed by Weigel [4]. With the exception of a value for C_p there is a complete set of values for the thermodynamic properties of radium iodate. The values are listed in Table 2 and show good agreement with the trend observed for the thermodynamic values for the other alkaline-earth iodates. An estimate of $188 \text{ J K}^{-1} \text{ mol}^{-1}$ was obtained for $C_p(\text{Ra}(\text{IO}_3)_2)$ based on the value for $C_p(\text{Ba}(\text{IO}_3)_2)$ and the trend in C_p for the alkaline-earth compounds.

$\text{Ra}(\text{IO}_3)_2(\text{aq})$

There are no reports for the thermodynamic properties of radium iodate in solution and there are insufficient data for the thermodynamic properties of the remaining alkaline-earth iodates as aqueous species for estimates to be based on trend analysis. There is a set of values for the thermodynamic properties of $\text{Ba}(\text{IO}_3)_2(\text{aq})$ and, since the thermodynamic values for the barium and radium iodates in the crystal phase are very similar, it is assumed that this similarity may be transferred to the aqueous phase, allowing the following values to be estimated: $\Delta H_f(\text{Ra}(\text{IO}_3)_2(\text{aq}))$, -979 kJ mol^{-1} ; $\Delta G_f(\text{Ra}(\text{IO}_3)_2(\text{aq}))$, -820 kJ mol^{-1} , $S(\text{Ra}(\text{IO}_3)_2(\text{aq}))$, $268 \text{ J K}^{-1} \text{ mol}^{-1}$.

$\text{Ra}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$

The preparation of $\text{Ra}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ has been discussed by Weigel [4]. As no values for thermodynamic properties have been reported for this compound, those listed in Table 2 were calculated using the additivity rule for hydrates and the following average increases for the addition of one molecule of water to an alkaline-earth iodate: $\Delta[\Delta H_f] = -294 \text{ kJ mol}^{-1}$; $\Delta[\Delta G_f] = -236 \text{ kJ mol}^{-1}$; $\Delta[S] = 36 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta[C_p] = 45 \text{ J K}^{-1} \text{ mol}^{-1}$. These values may be used to determine the thermodynamic properties of any hydrate of radium bromide.

RaS

The preparation of RaS has been discussed by Weigel [4] but there are no reported experimental values for its thermodynamic properties. The following estimates have been reported or were calculated: $\Delta H_f(\text{RaS})$, -446 kJ

mol^{-1} [30,31]; $\Delta G_f(\text{RaS})$, -423 kJ mol^{-1} [30]; $S(\text{RaS})$, $85 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(\text{RaS})$, 52 [KU] and $51 \text{ J K}^{-1} \text{ mol}^{-1}$ [36].

Ra(HS)₂

There are no reports for the preparation of *Ra(HS)₂*. Experimental thermodynamic data for this group of alkaline-earth compounds is limited to ΔH_f values of $\text{Ca(HS)}_2(\text{aq})$ and $\text{Ba(HS)}_2(\text{aq})$ [5]. There is an estimate of -548 J mol^{-1} for $\Delta H_f(\text{Ra(HS)}_2(\text{aq}))$ [30]. No estimates have been reported for the other thermodynamic properties and, in the absence of data for the other alkaline-earth compounds of this group, no correlations were made.

RaSO₃

There are no reports for the experimental preparation of radium sulphite. The following estimates for the thermodynamic properties of this compound have been reported or were calculated: $\Delta H_f(\text{RaSO}_3)$, -1180 [30,31], -1178 J mol^{-1} [44]; $\Delta G_f(\text{RaSO}_3)$, -1089 J mol^{-1} , as an estimate based on very limited data: $S(\text{RaSO}_3)$, $133 \text{ J K}^{-1} \text{ mol}^{-1}$ [45]; $C_p(\text{RaSO}_3)$, $96 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in values of estimates reported by Erdos [45] for the C_p of the other alkaline-earth sulphites.

RaSO₃ · nH₂O

There are no reports for the experimental preparation of hydrates of radium sulphite. There is a limited amount of data for hydrates of some of the other alkaline-earth sulphites [5]. The values probably follow the additivity rule for hydrates but the amount of data was insufficient to permit their estimation.

RaSO₄

The preparation of *RaSO₄* has been discussed by Weigel [4]. With the exception of a value for C_p there is a complete set of values for the thermodynamic properties of *RaSO₄* [5]. The values listed in Table 2 are in good agreement with the trend observed for the thermodynamic values for the other alkaline-earth sulphates. The following estimates have been reported or calculated for $C_p(\text{RaSO}_4)$, 104 [KU] and $102 \text{ J K}^{-1} \text{ mol}^{-1}$ [36]. Both values are in good agreement with the trend in values of C_p for the other alkaline-earth sulphates.

RaSO₄(aq)

With the exclusion of a value for C_p a complete set of thermodynamic data for *RaSO₄(aq)* [5] is included in Table 2. The data are in good

agreement with the general trend in values for the other alkaline-earth sulphates as aqueous species.

RaSO₄ · nH₂O

There are no reports for the preparation of hydrates of radium sulphate. The thermodynamic properties of the hydrates of beryllium, magnesium and calcium sulphate obey the additivity rule for hydrates and the following average increases were found for the addition of one molecule of water to an alkaline-earth sulphate: $\Delta[\Delta H_f] = -301 \text{ kJ mol}^{-1}$; $\Delta[\Delta G_f] = -243 \text{ kJ mol}^{-1}$; $\Delta[S] = 42 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta[C_p] = 42 \text{ J K}^{-1} \text{ mol}^{-1}$. These values may be used to determine the thermodynamic properties of any hydrate of radium sulphate.

Ra(HSO₄)₂

The preparation of *Ra(HSO₄)₂* has not been reported. No experimental values have been reported for any of the other alkaline-earth bisulphates. Wilcox [30] estimated a value of $-2326 \text{ kJ mol}^{-1}$ for $\Delta H_f(\text{Ra}(\text{HSO}_4)_2)$. There are no estimates for the other thermodynamic properties of this compound.

Other sulphur compounds of radium

No estimates have been reported for the other sulphur compounds of radium. There is only a very small amount of experimental data for the thermodynamic properties of the analogous sulphur compounds of the other alkaline-earths. The data that are available are limited to ΔH_f values and apply to thio or dithio salts as hydrates or as aqueous species [5]. Consequently, no correlations have been carried out for any other sulphur compounds of radium.

RaSe

The preparation of radium selenide has been discussed by Weigel [4] but there are no reported experimental values for the thermodynamic properties. The following estimates have been reported or were calculated: $\Delta H_f(\text{RaSe})$, -360 kJ mol^{-1} based on the trend in ΔH_f values for the other alkaline-earth selenides; $\Delta G_f(\text{RaSe})$, -350 kJ mol^{-1} based on the trend in ΔG_f values for other alkaline-earth selenides and the trend for the alkaline-earth sulphides; $S(\text{RaSe})$, $92 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in S values for the alkaline-earth oxides, sulphides and selenides; $C_p(\text{RaSe})$, 54 [KU] and $52 \text{ J K}^{-1} \text{ mol}^{-1}$ [36].

RaSeO₃

The preparation of radium selenite is discussed briefly by Weigel [4], but there are no reported experimental values for the thermodynamic properties of this compound. The experimental data for the thermodynamic properties of the selenites of the other alkaline-earths were insufficient to allow estimates to be made by the normal correlations. However, by combining the data for the sulphites, sulphates and selenites, a trend could be discerned which allowed the following estimates to be made: $\Delta H_f(\text{RaSeO}_3)$, $-1033 \text{ kJ mol}^{-1}$; $\Delta G_f(\text{RaSeO}_3)$, -970 kJ mol^{-1} ; $S(\text{RaSeO}_3)$, $174 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{RaSeO}_3)$, $100 \text{ J K}^{-1} \text{ mol}^{-1}$.

RaSeO₄

The preparation of radium selenate has been discussed by Weigel [4], but there are no experimental values for the thermodynamic properties of this compound. The following estimates have been reported: $\Delta H_f(\text{RaSeO}_4)$, -1176 [30,31], $-1178 \text{ kJ mol}^{-1}$ [46]; $\Delta G_f(\text{RaSeO}_4)$, $-1050 \text{ kJ mol}^{-1}$ [30]; $S(\text{RaSeO}_4)$, $180 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in S values for the alkaline-earth sulphates and selenates; $C_p(\text{RaSeO}_4)$, $108 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in C_p values for the alkaline-earth selenates.

Other selenium compounds of radium

There are no reports on the preparation of other selenium compounds of radium nor of estimates for theoretical selenium compounds of radium.

Tellurium compounds of radium

There are no reports on the preparation of tellurium compounds of radium. Thermodynamic data for tellurium compounds of the alkaline-earths are limited to a value for $\Delta H_f(\text{MgTe})$ and $S(\text{CaTe})$ [5], and are insufficient to enable correlations to be carried out for theoretical tellurium compounds of radium. Krestov [36] gave a value of $54 \text{ J K}^{-1} \text{ mol}^{-1}$ for $C_p(\text{RaTe})$, and a similar value is found by using the equation of Kubaschewski and Unal [7].

Polonium compounds of radium

As there are no reports on the preparation of polonium compounds of radium and no thermodynamic data for polonium compounds of the alkaline-earths, no correlations were made for radium compounds of polonium. Krestov [36] gave a value of $54 \text{ J K}^{-1} \text{ mol}^{-1}$ for $C_p(\text{RaPo})$.

$\text{Ra}(\text{N}_3)_2$

The preparation of radium azide was discussed briefly by Weigel [4], but there are no reported experimental values for the thermodynamic properties of this compound. The alkaline-earth azides become increasingly stable with increasing atomic number of the cation and ΔH_f , ΔG_f and S values of barium azide are available [5]. With limited information, the following estimates were made: $\Delta H_f(\text{Ra}(\text{N}_3)_2)$, -4 kJ mol^{-1} ; $\Delta G_f(\text{Ra}(\text{N}_3)_2)$, -170 kJ mol^{-1} ; $S(\text{Ra}(\text{N}_3)_2)$, $170 \text{ J K}^{-1} \text{ mol}^{-1}$. No estimate could be made for $C_p(\text{Ra}(\text{N}_3)_2)$.

 Ra_3N_2

The preparation of a radium nitride of uncertain stoichiometry was discussed briefly by Weigel [4] but there are no reported experimental values for the thermodynamic properties of this compound. A value of -535 kJ mol^{-1} was estimated for $\Delta H_f(\text{Ra}_3\text{N}_2)$ based on the trend in ΔH_f values for the equivalent alkaline-earth nitrides [4]. There are no data for the other thermodynamic properties of these compounds, so no estimates could be made for ΔG_f , S or C_p .

Other nitrides of radium

No other nitride of radium have been reported. However, the observed increase in the stability of alkaline-earth nitrides with increasing atomic number, exemplified by a measured value for $\Delta H_f(\text{Ba}_2\text{N})$, indicates that other radium nitrides could be expected.

 $\text{Ra}(\text{NH}_2)_2$

There have been no reports on the preparation of radium amide. A value of -331 kJ mol^{-1} was estimated for $\Delta H_f(\text{Ra}(\text{NH}_2)_2)$ [30]. This value is slightly higher than ΔH_f values for the other alkaline-earth amides. There are no data for other thermodynamic properties of the alkaline-earth amides, so no estimates could be made for ΔG_f , S or C_p .

 $\text{Ra}(\text{NO}_2)_2$

There are no reports on the experimental preparation of radium nitrite. The following estimate has been reported for $\Delta H_f(\text{Ra}(\text{NO}_2)_2)$: -774 J mol^{-1} [30,31]. In the absence of data for other thermodynamic properties of the alkaline-earth nitrites, no other correlations were possible for this compound.

$\text{Ra}(\text{NO}_3)_2$

The preparation of radium nitrate was discussed by Weigel [4]. With the exception of a value for C_p , there is a complete set of experimental values for the thermodynamic properties of $\text{Ra}(\text{NO}_3)_2$ [5]. These values are listed in Table 2 and are in good agreement with the trend observed for the thermodynamic values for the other alkaline-earth nitrates. The following estimates have been reported for $C_p(\text{Ra}(\text{NO}_3)_2)$: 155 [KU] and 153 J K⁻¹ mol⁻¹ [36]. Both values are in good agreement with the trend in values of C_p for the other alkaline-earth nitrates.

$\text{Ra}(\text{NO}_3)_2(\text{aq})$

With the exception of a value for C_p there is a complete set of thermodynamic data for $\text{Ra}(\text{NO}_3)_2(\text{aq})$ [5]. These values are listed in Table 2 and are in good agreement with the general trend in values for the other alkaline-earth sulphates as aqueous species.

$\text{Ra}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$

There are no reports on the preparation of hydrates of radium nitrate. There is an extensive range of thermodynamic data for hydrates of magnesium, calcium and strontium nitrates [5]. These hydrates obey the additivity rule of hydrates and the following average increases were found for the addition of one molecule of water to an alkaline-earth nitrate: $\Delta[\Delta H_f] = -301$ kJ mol⁻¹; $\Delta[\Delta G_f] = -246$ kJ mol⁻¹; $\Delta[S] = 43$ J K⁻¹ mol⁻¹; and $\Delta[C_p] =$ no data. These values may be used to determine the thermodynamic properties of any hydrate of radium nitrate.

Ra_3P_2

There are no reports on the preparation of radium phosphides and there are insufficient data on the other alkaline-earth phosphides to allow correlations to be made.

$\text{Ra}_3(\text{PO}_4)_2$

There are no reports on the preparation of radium orthophosphate. The following estimates were made for the thermodynamic properties of this compound: $\Delta H_f(\text{Ra}_3(\text{PO}_4)_2)$, -4164 kJ mol⁻¹ [Ta]; $\Delta G_f(\text{Ra}_3(\text{PO}_4)_2)$, -3974 kJ mol⁻¹ [Ta]. These values are in good agreement with the general trend of ΔH_f and ΔG_f values for the other alkaline-earth orthophosphates. There are insufficient data to allow correlations to be made for $S(\text{Ra}_3(\text{PO}_4)_2)$ and $C_p(\text{Ra}_3(\text{PO}_4)_2)$.

Other phosphates of radium

The correlations of Tardy and Vieillard [18] permit the determination of ΔH_f and ΔG_f values for metaphosphates, pyrophosphates, tripolyphosphates and tetrapolyphosphates. However, there are insufficient data from the other alkaline-earth phosphates to support the correlations within the alkaline-earth group.

Radium compounds of arsenic

There have been no reports on the formation of radium compounds of arsenic and the thermodynamic data for arsenic compounds of the other alkaline-earths are insufficient to allow satisfactory correlations to be made.

Radium compounds of antimony

There have been no reports on the formation of radium compounds of antimony and the thermodynamic data for antimony compounds of the other alkaline-earths are insufficient to allow satisfactory correlations to be made.

Radium compounds of bismuth

There have been no reports on the formation of radium compounds of bismuth and the thermodynamic data for bismuth compounds of the other alkaline-earths are insufficient to allow satisfactory correlations to be made.

RaC₂

There have been no reports on the preparation of radium carbide. There is very little information on the thermodynamic properties of the carbides of the other alkaline-earths. A value of -80 kJ mol^{-1} was estimated for $\Delta H_f(\text{RaC}_2)$ based on the trend in ΔH_f values for the other alkaline-earth carbides. Other thermodynamic properties of RaC_2 could not be estimated because of a lack of data.

RaCO₃

The preparation of radium carbonate has been discussed by Weigel [4]. No thermodynamic properties have been reported for this compound. The following estimates have been reported or were calculated: $\Delta H_f(\text{RaCO}_3)$, $-1222 \text{ kJ mol}^{-1}$ [30,31]; $\Delta G_f(\text{RaCO}_3)$, $-1142 \text{ kJ mol}^{-1}$ [Ta]; $S(\text{RaCO}_3)$, $123 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(\text{RaCO}_3)$, $85 \text{ J K}^{-1} \text{ mol}^{-1}$ [KU] [36].

Ra(HCO₃)₂

There have been no reports on the preparation of radium bicarbonate but a complete set of values for the thermodynamic properties has been reported for magnesium and barium bicarbonate in the aqueous state [5]. An estimate of $-1979 \text{ kJ mol}^{-1}$ has been reported for $\Delta H_f(\text{Ra}(\text{HCO}_3)_2)$ [30,31] but there are no thermodynamic data for the other alkaline-earth bicarbonates with which to compare this value. Lack of data prevented the estimation of other thermodynamic properties of *Ra(HCO₃)₂*.

RaC₂O₄

There have been no reports on the preparation of radium oxalate. An estimate of $-1410 \text{ kJ mol}^{-1}$ was reported for $\Delta H_f(\text{RaC}_2\text{O}_4)$ [30,31] which is in good agreement with the trend in ΔH_f values for the other alkaline-earth oxalates. Other thermodynamic properties of *RaC₂O₄* could not be estimated because of a lack of data.

Ra(HCO₂)₂

There have been no reports on the preparation of radium formate. An estimate of $-1376 \text{ kJ mol}^{-1}$ has been reported [30,31] for $\Delta H_f(\text{Ra}(\text{HCO}_2)_2)$ which is in good agreement with the trend in ΔH_f values for the other alkaline-earth formates. Other thermodynamic properties of *Ra(HCO₂)₂* could not be estimated because of a lack of data.

Ra(C₂H₃O₂)₂

The preparation of radium acetate was discussed briefly by Weigel [4]. An estimate of $-1498 \text{ kJ mol}^{-1}$ has been reported [30,31] for $\Delta H_f(\text{Ra}(\text{C}_2\text{H}_3\text{O}_2)_2)$ which is in good agreement with the trend in ΔH_f values for the other alkaline-earth acetates. Other thermodynamic properties of *Ra(C₂H₃O₂)₂* could not be estimated because of a lack of data.

Ra(CN)₂

There have been no reports on the preparation of radium cyanide. An estimate of -218 kJ mol^{-1} has been reported [30,31] for $\Delta H_f(\text{Ra}(\text{CN})_2)$ which is in good agreement with the trend in ΔH_f values for the other alkaline-earth cyanides. Other thermodynamic properties of *Ra(CN)₂* could not be estimated because of a lack of data.

RaCN₂

There have been no reports on the preparation of radium cyanamide. An estimate of -234 kJ mol^{-1} was made for $\Delta H_f(\text{RaCN}_2)$ based on the trend

in values for the other alkaline-earth cyanamides. Other thermodynamic properties of $RaCN_2$ could not be estimated because of a lack of data.

Ra(CNS)₂

There have been no reports on the preparation of radium thiocyanide. An estimate of -406 kJ mol^{-1} was reported [30,31] for $\Delta H_f(Ra(CNS)_2)$ but there are no thermodynamic data for the other alkaline-earth thiocyanides with which to compare this value. Other thermodynamic properties of $Ra(CNS)_2$ could not be estimated because of a lack of data.

RaSi₂

There have been no reports on the preparation of radium silicide. A variety of alkaline-earth silicides has been prepared but there is insufficient information on their thermodynamic properties to allow estimates to be made for any of the thermodynamic properties of $RaSi_2$.

RaSiO₃

There are no reports on the preparation of radium metasilicate. The following estimates have been reported or were calculated for the thermodynamic properties of this compound: $\Delta H_f(RaSiO_3)$, $-1577 \text{ kJ mol}^{-1}$ [30,31]; $\Delta G_f(RaSiO_3)$, -1540 [30], $-1537 \text{ kJ mol}^{-1}$ [Ta]; $S(RaSiO_3)$, $120 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(RaSiO_3)$, $91 \text{ K}^{-1} \text{ mol}^{-1}$ based on the trend in values for C_p of the other alkaline-earth metasilicates.

Ra₂SiO₄

There are no reports on the preparation of radium orthosilicate. The following estimates were made for the thermodynamic properties of this compound: $\Delta H_f(RaSiO_4)$, $-2268 \text{ kJ mol}^{-1}$ based on the trend in values for ΔH_f of the other alkaline-earth silicates; $\Delta G_f(Ra_2SiO_4)$, $-2268 \text{ kJ mol}^{-1}$ [Ta]; $S(RaSiO_3)$, $195 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(RaSiO_3)$, $136 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in values for C_p of the other alkaline-earth silicates.

Other radium silicate minerals

There are no estimates for other radium silicate minerals. Chen [47] published a method for the estimation of ΔG_f values of complex silicate minerals; this method could be applied to the radium analogues.

Ra(ReO₄)₂

There are no reports on the preparation of radium perrhenate. An estimate of $-2167 \text{ kJ mol}^{-1}$ was reported [30,31] for $\Delta H_f(Ra(ReO_4)_2)$. No

estimates have been reported for values of any of the other thermodynamic properties of this compound or of any other alkaline-earth perhenate. Consequently, the other thermodynamic properties could not be estimated.

RaCrO₄

The preparation of radium chromate was discussed by Weigel [4]. No values have been reported for the thermodynamic properties of this compound. The following estimates have been reported or were calculated: $\Delta H_f(\text{RaCrO}_4)$, $-1440 \text{ kJ mol}^{-1}$ based on the trend in values for ΔH_f of the other alkaline-earth chromates [5,48] and assuming that chromate is an analogue of sulphate; $\Delta G_f(\text{RaCrO}_4)$, $-1330 \text{ kJ mol}^{-1}$ [30]; $S(\text{RaCrO}_4)$, $160 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the value for $S(\text{BaCrO}_4)$ and assuming that chromate is an analogue of sulphate; $C_p(\text{RaCrO}_4)$, $118 \text{ J K}^{-1} \text{ mol}^{-1}$ [KU].

RaMoO₄

The preparation of radium molybdate was discussed by Weigel [4]. No experimental values have been reported for the thermodynamic properties of this compound. The following estimates have been reported or were calculated: $\Delta H_f(\text{RaMoO}_4)$, $-1570 \text{ kJ mol}^{-1}$ [49]; $\Delta G_f(\text{RaMoO}_4)$, $-1470 \text{ kJ mol}^{-1}$ [49]; $S(\text{RaMoO}_4)$, $157 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(\text{RaMoO}_4)$, $118 \text{ J K}^{-1} \text{ mol}^{-1}$ [KU].

RaWO₄

The preparation of radium tungstate was discussed by Weigel [4]. No experimental values have been reported for the thermodynamic properties of this compound. The following estimates have been reported or were calculated: $\Delta H_f(\text{RaWO}_4)$, $-1693 \text{ kJ mol}^{-1}$ [49]; $\Delta G_f(\text{RaWO}_4)$, $-1592 \text{ kJ mol}^{-1}$ [49]; $S(\text{RaWO}_4)$, $166 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(\text{RaWO}_4)$, $125 \text{ J K}^{-1} \text{ mol}^{-1}$ [KU].

RaV₂O₆

There are no reports on the preparations of radium vanadate and no estimates have been reported for the thermodynamic properties of this compound. There are insufficient data for other alkaline-earth vanadates to allow estimates of either $\Delta H_f(\text{RaV}_2\text{O}_6)$ or $\Delta G_f(\text{RaV}_2\text{O}_6)$. An estimate of $243 \text{ J K}^{-1} \text{ mol}^{-1}$ was obtained for $S(\text{RaV}_2\text{O}_6)$ [TM] and of $184 \text{ J K}^{-1} \text{ mol}^{-1}$ for $C_p(\text{RaV}_2\text{O}_6)$ based on the trend in values for C_p of the other alkaline-earth vanadates.

Ra₂V₂O₇

There are no reports on the preparation of radium pervanadate and no estimates have been reported for the thermodynamic properties of this compound. There are insufficient data for other alkaline-earth vanadates to allow estimates of either $\Delta H_f(Ra_2V_2O_7)$ or $\Delta G_f(Ra_2V_2O_7)$. An estimate of $290 \text{ J K}^{-1} \text{ mol}^{-1}$ was obtained for $S(Ra_2V_2O_7)$ [TM] and $226 \text{ J K}^{-1} \text{ mol}^{-1}$ for $C_p(Ra_2V_2O_7)$ based on the trend in values for C_p of the other alkaline-earth pervanadates.

RaTiO₃

There have been no reports on the preparation of radium titanate and no estimates have been reported for the thermodynamic properties of this compound. The following values have been estimated: $\Delta H_f(RaTiO_3)$, $-1640 \text{ kJ mol}^{-1}$ based on the trend in experimental values of ΔH_f for the other alkaline-earth titanates and assuming that the titanates are analogues of silicates; $\Delta G_f(RaTiO_3)$, $-1548 \text{ kJ mol}^{-1}$ estimated on the same basis as the ΔH_f value; $S(RaTiO_3)$, $123 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(RaTiO_3)$, $103 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in experimental values for C_p for the other alkaline-earth titanates.

Ra₂TiO₄

There have been no reports on the preparation of diradium titanate. The following estimates were made for the thermodynamic properties of this compound: $\Delta H_f(Ra_2TiO_4)$, $-2197 \text{ kJ mol}^{-1}$ based on the trend in experimental values for ΔH_f of the alkaline-earth titanates and assuming that the titanates are analogous of silicates; $\Delta G_f(Ra_2TiO_4)$, $-2092 \text{ kJ mol}^{-1}$ estimated on the same basis as the ΔH_f value; $S(Ra_2TiO_4)$, $214 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(Ra_2TiO_4)$, $160 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in experimental values for C_p for the other alkaline-earth titanates.

RaZrO₃

There have been no reports on the preparation of radium zirconate. The following estimates were made for the thermodynamic properties of this compound: $\Delta H_f(RaZrO_3)$, $-1785 \text{ kJ mol}^{-1}$ based on the trend in experimental values for ΔH_f of the other alkaline-earth zirconates and assuming that the zirconates are analogues of silicates; $\Delta G_f(RaZrO_3)$, $-1707 \text{ kJ mol}^{-1}$ estimated on the same basis as the ΔH_f value; $S(RaZrO_3)$, $134 \text{ J K}^{-1} \text{ mol}^{-1}$ [TM]; $C_p(RaZrO_3)$, $105 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the trend in experimental values for C_p of the other alkaline-earth zirconates.

RaCeO₃

The preparation of radium cerate was discussed briefly by Weigel [4]. No values have been reported for the thermodynamic properties of this compound or for any other alkaline-earth cerate. Consequently, thermodynamic properties could not be estimated.

RaBeF₄

The preparation of radium tetrafluoroberyllate was discussed by Weigel [4]. No values have been reported for the thermodynamic properties of this compound or of any other alkaline-earth tetrafluoroberyllate. Consequently, the thermodynamic properties could not be estimated.

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