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The Thermodynamic Hydrate Difference Rule (HDR) Applied to Salts of Carbon-Containing Oxyacid Salts and Their Hydrates: Materials at the Inorganic−Organic Interface[†]

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The thermodynamic hydrate difference rule (HDR) has previously been explored largely within the compass of inorganic solids. In this paper we extend its range by studying its application to carbon-containing oxyacid salts, which may be regarded as borderline hydrate-forming inorganic or organic material. We study in detail standard thermodynamic data as it appears in the National Bureau of Standards (NBS) tabulation for formate, carbonate, acetate, glycolate, and oxalate salt hydrates, finding the HDR to apply equally as well to these materials as it does to salts with solely inorganic parents. We use the resulting constants to predict thermodynamic quantities for some parent salts.

Introduction

The hydrate difference rule (HDR)[1−5] takes a number of (essentially equivalent) analytical forms:

$$P(n\text{-hydrate}) \approx P(\text{parent}) + n\theta_P(\mathrm{H_2O}) \qquad (1)$$

$$[P(m\text{-hydrate}) - P(n\text{-hydrate})] \approx (m - n)\theta_P(\mathrm{H_2O}) \qquad (2)$$

$$P(k\text{-hydrate}) + P(l\text{-hydrate})] \approx P(m\text{-hydrate}) + P(n\text{-hydrate}) \quad \text{with} \quad k + l = m + n \qquad (3)$$

$$P(k\text{-hydrate}) + P(l\text{-hydrate}')] \approx P(m\text{-hydrate}) + P(n\text{-hydrate}') \quad \text{with} \quad k + l = m + n \qquad (4)$$

where these equations, which are simply variations of one another, are expressions of the additivity of the corresponding thermodynamic quantities. *P* denotes a standard thermodynamic property, where *P*, interalia, can be $\Delta_f H^o$, $\Delta_f G^o$, or S^o_{298}. Equation 2 derives directly from eq 1.

In its most important role, the generalized thermodynamic difference rule (TDR)[1−5] provides a means whereby new or missing thermodynamic data can be inferred from established data. In use we consider the *difference* in the thermodynamic properties, *P*, of an hydrate, ($M_pX_q\cdot n\mathrm{H_2O}$) and its parent, ($M_pX_q$). That is, the "difference function", [*P*(*n*-hydrate) − *P*(parent)] when plotted versus *n* should be linear with the gradient, $\theta_P(\mathrm{H_2O})$. Values of $\theta_P(\mathrm{H_2O})$ are well-established and are reasonably constant throughout for all hydrates (whether single or multiple).

$$\theta_{H_f}(\mathrm{H_2O})/\mathrm{kJ\cdot mol^{-1}} \approx -298.6 \qquad (6)$$

$$\theta_{G_f}(\mathrm{H_2O})/\mathrm{kJ\cdot mol^{-1}} \approx -242.4 \qquad (7)$$

$$\theta_S(\mathrm{H_2O})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} \approx 40.9 \qquad (8)$$

We study in detail standard thermodynamic data as it appears in the NBS tabulation for formate, carbonate, acetate, glycolate, and oxalate salt hydrates, finding the HDR to apply equally as well to these materials as it does to salts with solely inorganic parents. Thus, the present paper further establishes this same consistency in $\theta_P(\mathrm{H_2O})$ for the borderline case of inorganic/organic salts of carbon-containing weak acids. We use the resulting constants to predict thermodynamic quantities for some parent salts.

Thermodynamic Data

Enthalpy of Formation Data. Table 1 lists data for the standard enthalpy of formation, $\Delta_f H^o$, taken from the National

Table 1a. Formation Enthalpies and Mean Hydrate Enthalpy Contributions for Formates[a]

formate salt hydrate, $\Delta_f H^o$	kJ·mol−1	parent formate salt, $\Delta_f H^o$ kJ·mol−1	*n*	difference function $[\Delta_f H^o(\text{hydrate,s}) - \Delta_f H^o(\text{parent,s})]/n$ kJ·mol−1
$\mathrm{Na(CHO_2)_2\cdot 2H_2O}$ (s)	−1259	−666.5	2	−296.3
$\mathrm{Na(CHO_2)_2\cdot 3H_2O}$ (s)	−1552	−666.5	3	−295.2
$\mathrm{Sr(CHO_2)_2\cdot 2H_2O}$ (s)	−1990.7	−1393.3	2	−298.7
$\mathrm{Mn(CHO_2)_2\cdot 2H_2O}$ (s)	−1645.1	−1044.7	2	−300.2
$\mathrm{Cu(CHO_2)_2\cdot 4H_2O}$ (s)	−1961	−781.2	4	−295.0
$\mathrm{Zn(CHO_2)_2\cdot 2H_2O}$ (s)	−1584.9	−986.6	2	−299.2
$\mathrm{UO_2\cdot(CHO_2)_2\cdot H_2O}$ (s)	−2157.1	−1849.7	1	−307.4
			Mean	−298.8
			Std. Dev.	4

[a] The mean difference function over all water molecules in these formates is −297.6 kJ·mol−1.

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Table 1b. Formation Enthalpies and Mean Hydrate Enthalpy Contributions for Carbonates[a]

carbonate salt hydrate, $\Delta_f H^o$		parent carbonate salt, $\Delta_f H^o$		difference function $[\Delta_f H^o(\text{hydrate,s}) - \Delta_f H^o(\text{parent,s})]/n$
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	n	$kJ \cdot mol^{-1}$
$Na_2CO_3 \cdot H_2O$[b]	−1431.26	−1130.68	1	−300.6
$Na_2CO_3 \cdot 7H_2O$[b]	−3199.96	−1130.68	7	−295.6
$Na_2CO_3 \cdot 10H_2O$[b]	−4081.32	−1130.68	10	−295.1
$K_2CO_3 \cdot 1.5H_2O$[b]	−1609.2	−1151.02	1.5	−305.5
$Rb_2CO_3 \cdot H_2O$	−1448.5	−1136	1	−312.5
$Rb_2CO_3 \cdot 1.5H_2O$	−1604.4	−1136	1.5	−312.3
$Rb_2CO_3 \cdot 3H_2O$	−2048.1	−1136	3	−304.0
$Cs_2CO_3 \cdot 3H_2O$	−2048.1	−1139.7	3	−302.8
			Mean	−303.5
			Std. Dev.	7
$Cs_4H_2(CO_3)_3 \cdot 10H_2O$	−10674.5	(−7639)[c]	10	
$Cs_4H_2(CO_3)_3 \cdot 17.5H_2O$	−12963.7	(−7652)[c]	17.5	

[a] The mean difference function over all water molecules in these carbonates is −299.3 $kJ \cdot mol^{-1}$. [b] "G−H-S relaxed" values, implying that the entropies are inconsistent (within the expected accuracy) with Gibbs energy and enthalpy. [c] Estimated parent enthalpy, using $\Delta_f H^o(\text{parent,s}) \approx \Delta_f H^o(\text{hydrate,s}) - n\theta_{H_f}(H_2O)$ with $\theta_{H_f}(H_2O) = -303.5$ $kJ \cdot mol^{-1}$. The constancy of the estimated parent enthalpies is to be noted.

Table 1c. Formation Enthalpies and Mean Hydrate Enthalpy Contributions for Acetates[a]

acetate salt hydrate, $\Delta_f H^o$		parent acetate salt, $\Delta_f H^o$		difference function $[\Delta_f H^o(\text{hydrate,s}) - \Delta_f H^o(\text{parent,s})]/n$
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	n	$kJ \cdot mol^{-1}$
$NaCH_3COO \cdot 3H_2O$ (s)	−1603.3	−708.81	3	−298.2
$Ca(CH_3COO)_2 \cdot H_2O$ (s)	−1772.3	−1479.5	1	−292.8
$Sr(CH_3COO)_2 \cdot 0.5H_2O$ (s)	−1631.8	−1487.4	0.5	−288.8
$Ba(CH_3COO)_2 \cdot 3H_2O$ (s)	−2369	−1484.5	3	−294.8
$Mn(CH_3COO)_2 \cdot 4H_2O$ (s)	−2338	−1148.1	4	−297.5
$Cu(CH_3COO)_2 \cdot H_2O$ (s)	−1189.1	−893.3	1	−295.8
$Zn(CH_3COO)_2 \cdot H_2O$ (s)	−1376.1	−1078.6	1	−297.5
$Zn(CH_3COO)_2 \cdot 2H_2O$ (s)	−1672.3	−1078.6	2	−296.9
$Pb(CH_3COO)_2 \cdot 3H_2O$ (s)	−1851.5	−963.83	3	−295.9
$UO_2 \cdot (CH_3COO)_2 \cdot 2H_2O$ (s)	−2558.9	−1963.55	2	−297.7
			Mean	−295.6
			Std. Dev.	3

[a] The mean difference function over all water molecules in these acetates is −296.4 $kJ \cdot mol^{-1}$.

Table 1d. Formation Enthalpies and Mean Hydrate Enthalpy Contributions for Glycolates[a]

glycolate salt hydrate, $\Delta_f H^o$		parent glycolate salt, $\Delta_f H^o$		difference function $[\Delta_f H^o(\text{hydrate,s}) - \Delta_f H^o(\text{parent,s})]/n$
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	n	$kJ \cdot mol^{-1}$
$Na(CH_2OHCOO)_2 \cdot 0.5H_2O$ (s)	−1048.9	−900.8	0.5	−296.2
$K(CH_2OHCOO)_2 \cdot 0.5H_2O$ (s)	−1064.4	−907.9	0.5	−313.0
$Mg(CH_2OHCOO)_2 \cdot 2H_2O$ (s)	−2348.1	−1750.6	2	−298.8
$Ca(CH_2OHCOO)_2 \cdot 3H_2O$ (s)	−2736.3	−1856	3	−293.4
$Ca(CH_2OHCOO)_2 \cdot 5H_2O$ (s)	−3311.2	−1856	5	−291.0
$Zn(CH_2OHCOO)_2 \cdot H_2O$ (s)	−1767.3	−1466.9	1	−300.4
			Mean	−298.8
			Std. Dev.	8

[a] The mean difference function over all water molecules in these glycolates is −294.8 $kJ \cdot mol^{-1}$.

Bureau of Standards (NBS) database[6] for formate salt hydrates (divalent $M(HCO_2)_2 \cdot nH_2O$); carbonate salt hydrates (monovalent $M_2CO_3 \cdot nH_2O$, divalent $MCO_3 \cdot nH_2O$, and bicarbonate $Cs_4H_2(CO_3)_3 \cdot nH_2O$)); acetate salt hydrates (monovalent $MCH_3COO \cdot nH_2O$ and divalent $M(CH_3COO)_2 \cdot nH_2O$); glycolate salt hydrates (divalent $M(CH_2OHCOO)_2 \cdot nH_2O$); and oxalate salt hydrates (bioxalate $NaHC_2O_4 \cdot nH_2O$, divalent $MC_2O_4 \cdot nH_2O$, and tervalent $M_2(C_2O_4)_3 \cdot nH_2O$); and, where available, for the corresponding parent salts: $M(HCO_2)_2$; M_2CO_3, MCO_3; MCH_3COO, $M(CH_3COO)_2$; $M(CH_2OHCOO)_2$; and MC_2O_4, $M_2(C_2O_4)_3$.

The tables for these five sets of oxyacid salts demonstrate excellent constancy in the enthalpy contribution of hydrated water ($\theta_{H_f}(H_2O)$) to the total enthalpy of the hydrates. The mean value across the whole set of values listed here is −300.3 $kJ \cdot mol^{-1}$, compared with our general inorganic value of −298.6 $kJ \cdot mol^{-1}$ (eq 6).

Gibbs Energy of Formation Data. Table 2 lists the only Gibbs energy data to be found from the NBS database[6] for the carbon-containing oxyacid hydrates discussed above. No Gibbs energy data are available for the oxalate parent salts nor for formate, carbonate, acetate, or glycolate salt hydrates or for their parents.

Table 1e. Formation Enthalpies and Mean Hydrate Enthalpy Contributions for Oxalates[a]

oxalate salt hydrate, $\Delta_f H^o$		parent oxalate salt, $\Delta_f H^o$		difference function $[\Delta_f H^o\text{ (hydrate,s)} - \Delta_f H^o\text{(parent,s)}]/n$
kJ·mol^{-1}		kJ·mol^{-1}	n	kJ·mol^{-1}
$(COOH)_2 \cdot 2H_2O$ (s)	−1426.7	−827.2(oxalic acid)	2	−299.8
$(NH_4)_2C_2O_4 \cdot H_2O$ (s)	−1425.5	−1123	1	−302.5
$NaHC_2O_4 \cdot H_2O$ (s)	−1384.1	−1082	1	−302.1
$K_2C_2O_4 \cdot H_2O$ (s)	−1644.7	−1346.8	1	−297.9
$CaC_2O_4 \cdot H_2O$ (s)	−1674.86	−1360.6	1	−314.3
$BaC_2O_4 \cdot 0.5H_2O$ (s)	−1528.8	−1368.6	0.5	−320.4
$BaC_2O_4 \cdot 2H_2O$ (s)	−1971.1	−1368.6	2	−301.3
$BaC_2O_4 \cdot 3.5H_2O$ (s)	−2412.5	−1368.6	3.5	−298.3
$MnC_2O_4 \cdot 2H_2O$ (s)	−1628.4	−1028.8	2	−299.8
$MnC_2O_4 \cdot 3H_2O$ (s)	−1920.9	−1028.8	3	−297.4
$FeC_2O_4 \cdot 2H_2O$ (s)	−1482.4	(−873)[b]	2	
$Ce_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−6782	(−3736)[b]	10	
$Pr_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5920	(−2874)[b]	10	
$Nd_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−6782	(−3736)[b]	10	
$UO_2 \cdot C_2O_4 \cdot H_2O$ (s)	−2112	−1796.9	1	−315.1
$UO_2 \cdot C_2O_4 \cdot 3H_2O$ (s)	−2715.4	−1796.9	3	−306.2
			Mean	−304.6
			Std. Dev.	8

[a] The mean difference function over all water molecules in these oxalates is −302.3 kJ·mol^{-1}. [b] No data for the parent oxalate are available. Estimation: $\Delta_f H^o\text{(parent,s)} \approx \Delta_f H^o\text{(hydrate,s)} - n\theta_{H_f}(H_2O)$.

Table 2. Gibbs Energy Formations for Lanthanide Oxalate Hydrates (Including Yttrium) and Estimates of Parent Values

oxalate salt hydrate, $\Delta_f G^o$			parent oxalate estimate[a]
kJ·mol^{-1}		n	kJ·mol^{-1}
$Y_2(C_2O_4)_3 \cdot 9H_2O$ (s)[b]	−5705.5	9	−3513
$La_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5915	10	−3479
$Ce_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5903	10	−3467
$Nd_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5907	10	−3471
$Sm_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5899	10	−3463
$Gd_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5886	10	−3450
$Tb_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5865	10	−3429
$Dy_2(C_2O_4)_3 \cdot 10H_2O$ (s)	−5890	10	−3454
$Er_2(C_2O_4)_3 \cdot 6H_2O$ (s)	−4949	6	−3487
$Yb_2(C_2O_4)_3 \cdot 5H_2O$ (s)	−4656	5	−3438
Std. Dev.	19 (0.6 %)	Mean	−3460

[a] Estimate: $\Delta_f G^o[M_2(C_2O_4)_3,s] = \Delta_f G^o[M_2(C_2O_4)_3 \cdot nH_2O,s] - 243.6n(H_2O)$, based on Figure 1 data. [b] $Y_2(C_2O_4)_3 \cdot 9H_2O$ has been omitted from the linear regression as a nonlanthanide. However, the Gibbs energy of its parent has been estimated on the same basis (cf. Figure 1).

We note that the thermodynamic data for the lanthanide oxalates are likely to be very similar. We test this observation by plotting $\Delta_f G^o[M_2(C_2O_4)_3 \cdot nH_2O,s]$ against $n(H_2O)$, in Figure 1.

The least-squares fitted line in Figure 1 has the formula $\Delta_f G^o[M_2(C_2O_4)_3 \cdot nH_2O,s]/\text{kJ} \cdot \text{mol}^{-1} = -243.6n - 3460.2$. The slope has a value which is essentially the same as our standard value of $\theta_{G_f}(H_2O)/\text{kJ} \cdot \text{mol}^{-1} \approx -242.4$ (eq 7). On this basis, we can confidently assert that the HDR is obeyed by these materials. Consequently, we can estimate the Gibbs energies of formation of the unhydrated parents by subtracting the hydrate contributions. These are listed in the final column of Table 2. The small standard deviation of 0.6 % confirms our initial assumption of the very similar thermodynamics of the lanthanide oxalates.

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This work was undertaken following the suggestion of an anonymous reviewer of the accompanying paper[5] in this Rowlinson Festschrift.

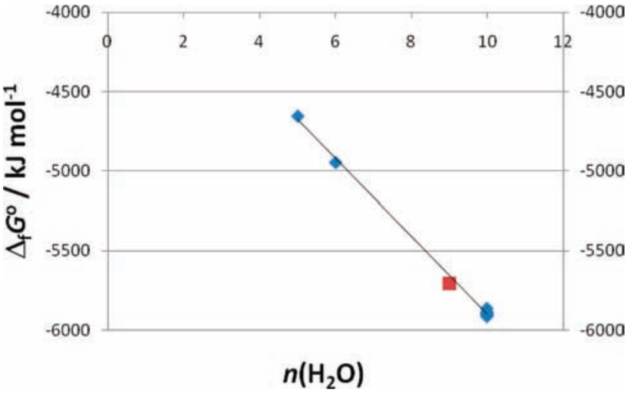

Figure 1. Plot of $\Delta_f G^o[M_2(C_2O_4)_3 \cdot nH_2O,s]$ against $n(H_2O)$ for the nine lanthanide oxalates in Table 2 (diamonds). The least-squares fitted line has the analytical form $\Delta_f G^o[M_2(C_2O_4)_3 \cdot nH_2O,s]/\text{kJ} \cdot \text{mol}^{-1} = -243.6n - 3465.5$; $R^2 = 0.999$. The data point for $Y_2(C_2O_4)_3 \cdot 9H_2O$ (s) is shown by the square.

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