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A simplification of gas clathrate hydrate thermochemistry using the Thermodynamic Difference Rule (TDR). Part 1. Generation of particularly simple forms for standard thermodynamic parameters for specific hydrates

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ABSTRACT

The Thermodynamic Difference Rule (TDR) adopts a particularly simple form when the enthalpy of formation of the "parent" atom/molecule within a clathrate hydrate is in its standard reference state at 298 K and 101.3 kPa (1 atm). In this case the simple form: $\Delta_f H^o = kn$ emerges for the standard formation data, where k is a numerical constant (=$\Theta_{Hf}(\mathrm{H_2O, s - g})$) and n is the number of moles of water present in the formula unit of the clathrate hydrate. The specific form is are: $\Delta_f H^o(\mathrm{M_pX_q.nH_2O, s})/\mathrm{kJ\ mol^{-1}} \approx \Theta_{Hf}(\mathrm{H_2O, s - g})\mathrm{n} = -296.1\ \mathrm{n}$ which is capable of offering predictions for standard thermodynamic data for a whole host of clathrate hydrates for which there isn't much or any experimental values. Moreover these data are predicted almost to within experimental error.

Another new result emerges, not previously reported, in that linear relationships with n are also found to exist for ΔH_{diss} for the dissociation process: $\mathrm{M_pX_q.nH_2O(s) \rightarrow nH_2O(l) + MpX_q(g)}$ and ΔH_{diss}' for the process: $\mathrm{M_pX_q.nH_2O(s) \rightarrow nH_2O(s, ice) + M_pX_q(g)}$ such that: $\Delta H_{diss}/\mathrm{kJ\ mol^{-1}} \approx 10.3\,n$ and ΔH_{diss}'/kJ $\mathrm{mol^{-1}} \approx 4.3\,n$.

Since no data exist for $\Delta_f G^o(\mathrm{M_pX_q.nH_2O, s})$ or $S^o_{298}(\mathrm{M_pX_q.nH_2O, s})$ in the literature, we further conjecture that, in accordance with previous studies, the equations: $\Delta_f G^o(\mathrm{M_pX_q.nH_2O, s})/\mathrm{kJ\ mol^{-1}} \approx \Theta_{Gf}(\mathrm{H_2O, s - g})\mathrm{n} = -242\ \mathrm{n}$ and $S^o_{298}(\mathrm{M_pX_q.nH_2O, s})/JK^{-1}\mathrm{mol^{-1}} \approx \Theta_{So}(\mathrm{H_2O, s - g})\mathrm{n} = 41\ \mathrm{n}$. could reasonably be anticipated to predict these unknown values for which no data are yet reported. The ability of TDR to tease out simple empirical relationships which have not been noticed previously amounts to a considerable simplification of this area of thermochemistry and provides the means of quick access estimation of (accurate) standard thermodynamic parameters for clathrate hydrates in the category studied here.

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1. Introduction

The Thermodynamic Difference Rule (TDR) [1–8] has proved remarkably successful in predicting the standard thermodynamic properties of inorganic hydrates, yielding results whose accuracy is invariably close to that of experiment. It is remarkable in the fact that it applies across the board to any inorganic species and its constant term Θ, only changes when the specific target thermodynamic parameter is altered. The procedure is simple to use, suitable for non–specialists and requires little more than a hand calculator to operate. In cases where hydrate thermodynamic data are sparse or even non–existent the TDR offers an ideal way to estimate this missing data as was demonstrated in our recent study [1] of uranium (IV) salts and their hydrates. In this paper the TDR is applied to clathrate hydrates and is found to be capable of revealing a number of extremely simple thermodynamic relationships which connect thermodynamic data to the number of water molecules, n, present in the formula unit of the hydrates. Such relationships are new, having not previously been noted and when tested using experimental data are able to identify deficiencies in that data so extending the power of the TDR technique.

A general inorganic hydrate is defined as a material with formula $\mathrm{M_pX_q.nH_2O}$ which is derived, in turn, from an inorganic "parent" (anhydrous) compound of formula $\mathrm{M_pX_q}$ for which $n = 0$. For such compounds the Thermodynamic Difference Rule takes the form:

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$$[\Delta P(\mathrm{M_pX_q.nH_2O,s}) - \Delta P(\mathrm{M_pX_q,s})] \approx n_P(H_2\mathrm{O,s{-}s}) + \mathrm{nH_2O} \qquad (1)$$

where $\Theta_P(\mathrm{H_2O,s-s})$ is a constant with s–s indicating that the hydrate and parent are both in their solid states, indicated by s. n represents the number of water molecules in the formula unit of the gas clathrate hydrate. For gas clathrate hydrates $\Theta_P(\mathrm{H_2O,s{-}s})$ would be modified to $\Theta_P(\mathrm{H_2O,s{-}g})$ – although its magnitude hardly changes – and $\Delta P(\mathrm{M_pX_q,s})$ is changed to $\Delta P(\mathrm{M_pX_q,g})$. $\Delta P(\mathrm{M_pX_q.nH_2O,s})$ represents the thermodynamic property of the hydrate and $\Delta P(\mathrm{M_pX_q,g})$ the same thermodynamic property of the anhydrous "parent" material, whilst ΔP can be $\Delta_f H^o/\mathrm{kJ\ mol^{-1}}$, $\Delta_f G^o/\mathrm{kJ\ mol^{-1}}$,$S^o_{298}/\mathrm{J\ K^{-1}\ mol^{-1}}$, $C^o_p/\mathrm{J\ K^{-1}\ mol^{-1}}$ *etc.* n is the number of water molecules possessed by the hydrate which can, itself, be a non–integer.

Water forms gas (clathrate) hydrates [9] when water is frozen in the presence of gaseous Ar(g), Kr(g), Cl_2(g), N_2(g), O_2(g), SO_2(g), CO_2(g), CH_3Cl(g), and so on; the gaseous CH_4(g) hydrate occurs naturally. Clathrate hydrates can be formed also with *liquid* Br_2(l). The gases Ar, Kr, Cl_2, N_2 and O_2 are in their standard reference states at 298K and 1 atm and so have zero enthalpies and zero free energies of formation, so too has Br_2 liquid and for these species we can write:

$$\begin{aligned}\Delta_f H^o(Ar,g) &= \Delta_f H^o(Kr,g) = \Delta_f H^o(Cl_2,g) = \Delta_f H^o(N_2,g)\\ &= \Delta_f H^o(O_2,g) = \Delta_f H^o(Br_2,l) = 0 \qquad (2)\end{aligned}$$

$$\begin{aligned}\Delta_f G^o(Ar,g) &= \Delta_f G^o(Kr,g) = \Delta_f G^o(Cl_2,g) = \Delta_f G^o(N_2,g)\\ &= \Delta_f G^o(O_2,g) = \Delta_f G^o(Br_2,l) = 0 \qquad (3)\end{aligned}$$

and in such cases the TDR as given in Eq. (1) now reduces to the particularly simple form:

$$\Delta P(M_pX_q.nH_2O,s) \approx n\Theta_P(H_2O,s{-}g) \qquad (4)$$

since $\Delta P(\mathrm{M_pX_q,g})$ is effectively zero. In the case of Br_2(l) the TDR reduces similarly to:

$$\Delta P(M_pX_q.nH_2O,s) \approx n\Theta_P(H_2O,s{-}l) \qquad (5)$$

In this paper we explore these simple relationships for $\Delta P = \Delta_f H^o$ and $\Delta_f G^o$ and test their applicability by comparison with experimentally derived data. Since other gas hydrate forming compounds like SO_2(g), CO_2(g), CH_3Cl(g) and CH_4(g) have finite (non–zero) values for $\Delta_f H^o(\mathrm{M_pX_q,g})$ and $\Delta_f G^o(\mathrm{M_pX_q,g})$ and therefore do not obey the simple form of Eq. (4) but rather follow the extended form of the TDR Eq. (1), we shall not concern ourselves with these latter hydrates any further in this paper.

2. Experimental sources of data: Standard enthalpy of formation and standard Gibbs energy of formation for gas hydrates

2.1. Enthalpies of dissociation of clathrate hydrates as sources of standard enthalpy of formation data

Two types of dissociation process have been studied for gas hydrates over the past 50 years [10]. The first process, denoted by H = L + G or (hlg) and whose dissociation enthalpy is designated as $\boldsymbol{\Delta H_{diss}}$ corresponds to the process:

$$\mathrm{M_pX_q.nH_2O(s) \rightarrow nH_2O(l) + M_pX_q} \qquad (6)$$

whilst the second process, denoted by H = I + G or (hig) and having dissociation enthalpy, $\boldsymbol{\Delta H_{diss}}$' is:

$$\mathrm{M_pX_q.nH_2O(s) \rightarrow nH_2O(s,ice) + M_pX_q} \qquad (7)$$

for which at 298 K and 101.3 kPa (1 atm) pressure we can write:

$$\begin{aligned}\Delta H_{\mathrm{diss}} &= \Delta_f H^o(\mathrm{M_pX_q,g}) + \mathrm{n}\ \Delta_f H^o(\mathrm{H_2O,l})\\ &\quad - \Delta_f H^o(\mathrm{M_pX_q.nH_2O,s})\\ &= [\Delta_f H^o(\mathrm{M_pX_q,g}) - \Delta_f H^o(\mathrm{M_pX_q.nH_2O,s})] - 285.8\ \mathrm{n} \qquad (8)\end{aligned}$$

having inserted the value for $\Delta_f H^o(\mathrm{H_2O,l})/\mathrm{kJ\ mol^{-1}} = -285.8$ [18]. Further [14] we have:

$$\begin{aligned}\Delta_f H^o(\mathrm{H_2O,s,ice})/\mathrm{kJ\ mol^{-1}} &= \Delta_f H^o(\mathrm{H_2O,l}) - \Delta_{\mathrm{fus}} H^o(\mathrm{ice})\\ &= \Delta_f H^o(\mathrm{H_2O,l}) - 6.010\\ &= -291.81 \qquad (9)\end{aligned}$$

and then:

$$\begin{aligned}\Delta H_{\mathrm{diss}}{}' &= \Delta_f H^o(\mathrm{M_pX_q.g}) + \mathrm{n}\ \Delta_f H^o(\mathrm{H_2O,s,ice})\\ &\quad - \Delta_f H^o(\mathrm{M_pX_q.nH_2O,s})\\ &= [\Delta_f H^o(\mathrm{M_pX_q.g}) - \Delta_f H^o(\mathrm{M_pX_q.nH_2O,s})] - 291.8\ \mathrm{n} \qquad (10)\end{aligned}$$

A large amount of dissociation equilibrium data has been summarised in the literature by Sloan [11] and Berecz and Balla–Achs [9]. Handa et al. [12] and Handa [13–16] and are attributed by Yoon et al. [10] to have mounted "a thorough *and correct* investigation" over a wide range of temperatures, using an automated Tian–Calvet heat–flow calorimeter. This comment implies that not all determinations of enthalpy of dissociation can be relied on and we shall return to this later. When discussing clathrate hydrates ΔH_{diss} and ΔH_{diss}' are almost always determined from the study of three phase equilibria by use of the Claperyron equation [20]. A differential scanning calorimeter (DSC) can also be used as can an isothermal microcalorimeter [10].

Using Eqs. (8) and (10) and the fact that:

$$\Delta_f H^o(\mathrm{M_pX_q,g})/\mathrm{kJ\ mol^{-1}} = 0 \qquad (11)$$

for the hydrates considered in this paper, it can be seen that thermodynamically:

$$\Delta H_{diss}/\mathrm{kJ\ mol^{-1}} = \Delta H'_{diss} + 6.01\ n \qquad (12)$$

Also by virtue of Eqs. (8), (10) and (11), $\Delta_f H^o$ $(\mathrm{M_pX_q}.n\mathrm{H_2O,s})$ can be determined from experimental measurements of either ΔH_{diss} or ΔH_{diss}' using:

$$\Delta_f H^o(\mathrm{M_pX_q}.n\mathrm{H_2O,s})/\mathrm{kJ\ mol^{-1}} = -\Delta H_{diss} - 285.8\ n \qquad (13)$$

and

$$\Delta_f H^o(\mathrm{M_pX_q}.n\mathrm{H_2O,s})/\mathrm{kJ\ mol^{-1}} = -\Delta H_{diss}{}' - 291.8\ n \qquad (14)$$

Results derived from experimentally determined dissociation data are summarised in Table 1.

2.2. Russian literature experimental sources of $\Delta_f H^o(M_pX_q.nH_2O,s)$ data

A second direct source of $\Delta_f H^o(\mathrm{M_pX_q}.n\mathrm{H_2O,s})$ for gas hydrates comes from a thermochemical database contained within a thesis [21] sent from Russia to the author in the late 60s by Professor S. A. Mamulov. This is the only direct source known to me of experimental standard thermochemical data for the standard state parent gas hydrates of interest in this paper.

Results derived from the thesis are summarised in Table 2.

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