A simplification of gas clathrate hydrate thermochemistry using the Thermodynamic Difference Rule (TDR). Part 2. General Hydrates

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ABSTRACT

For Gas Hydrates, $M_p X_q.nH_2O$, available experimental standard enthalpy of formation data, $\Delta_f H^o(M_p X_q.nH_2O, s)$, are fairly sparse and for standard Gibbs energy of formation, $\Delta_f G(M_p X_q.nH_2O, s)$ and standard entropy, $S^o_{298}(M_p X_q.nH_2O, s)$ has never been directly determined experimentally for any gas clathrate hydrate. Using the Thermodynamic Difference Rule, TDR we are, however, able to rectify this deficiency and provide three simple equations:

$$[\Delta_f H^o(M_p X_q.nH_2O, s) - \Delta_f H^o(M_p X_q, g)]/kJ\ mol^{-1} = -295.7n \quad (R^2 = 0.9998; N = 6)$$

$$[\Delta_f G^o(M_p X_q.nH_2O, s) - \Delta_f G^o(M_p X_q, g)]/kJ\ mol^{-1} = -242n$$

$$[S^o_{298}(M_p X_q.nH_2O, s) - S^o_{298}(M_p X_q, g)]/J\ K^{-1}\ mol^{-1} \approx 41n$$

capable of providing reliable estimates of these thermodynamic quantities for the entire suite of clathrate hydrates, always provided that the corresponding data for the gas molecules, $M_p X_q$ is known. As a result of these Difference Rule derived equations it emerges that the standard enthalpy, free energy and entropy of gas clathrate hydrates are, each, solely dependent on the number of moles of water, n, per formula unit. This is a new observation. The two enthalpies of dissociation of the hydrates for the processes (H = L + G): $\Delta H_{diss} = 9.9n$ kJ mol^{-1} and for (H = I + G): $\Delta H'_{diss} = 3.9n$ kJ mol^{-1} are also predicted by TDR to be a linear function of n. These results, which are discussed, are broadly consistent with those found in Part 1. A sample predictive calculation is given for $\Delta_f G^o$ and S^o_{298} for $CO_2 \cdot 6H_2O$.

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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 usually comparable to that of experiment. The TDR is also remarkable in the fact that it applies, across the board, to any inorganic species and its constant term $\Theta_P(H_2O)$ only changes when the nature of the specific target thermodynamic parameter, P, is altered, for example from enthalpy to free energy. The calculations are simple to make, suitable for non–specialists and require little more than a hand calculator or EXCEL spreadsheet to carry out. In cases where hydrate thermodynamic data are sparse or even non–existent the TDR offers an ideal way to estimate this missing data. In part 1 [9] specific hydrates, $M_p X_q.nH_2O$ for which the par-

ent, $M_p X_q$ consisted of an inert gas atom or a molecule in its standard reference state such that:

$$\Delta_f H^o(M_p X_q, g)/kJ\ mol^{-1} = 0 \quad (1)$$

were investigated.

The results were exemplary, showing exceedingly close agreement to the experimentally known values (always less than 1% in error and for most of the time considerably less than this) and also confidently able to generate values for clathrates obeying Eq. (1) and not having been previously studied. In the present paper we centre on clathrate hydrates for which the constraint of Eq. (1) does not apply and the gaseous parent molecule, $M_p X_q$ has a finite value for $\Delta_f H^o(M_p X_q, g)$.

1.1. Gas hydrates

A general hydrate is defined as a material with formula $M_p X_q.nH_2O$ which is derived, in turn, from an inorganic "parent"

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Nomenclature

P any standard thermodynamic property

$\Theta_P(H_2O)$ proportionality constant (in kJ mol^{-1}) relating the thermodynamic property, P to n

n   number of water molecules *in the hydrate formula unit*. *e.g.* $M_pX_q.nH_2O$

M_pX_q general formula for the gas or liquid clathrate host. *e.g.* Ar, Kr, Cl_2, N_2, O_2, Br_2

$\Delta_f H^o(M_pX_q, s)$/kJ mol^{-1} standard enthalpy of formation (in kJ·mol^{-1}) of the parent gaseous molecule, M_pX_q within the clathrate hydrate $M_pX_q.nH_2O$

$\Delta_f H^o(M_pX_q nH_2O, s)$/kJ mol^{-1} standard enthalpy of formation (in kJ·mol^{-1}) of the clathrate hydrate $M_pX_q.nH_2O$

$\theta_{Hf}(H_2O, s-g)$ proportionality constant (in kJ mol^{-1}) relating the thermodynamic property, $\Delta_f H^o$ to n.s–g signifies that the gas hydrate is a solid (s) *e.g.* $N_2.\underline{6.28}H_2O$ (s) and the clathrate host is in gaseous form (g) *e.g.* $N_2(g)$.

ΔH_{diss} enthalpy change (in kJ·mol^{-1}) for the process in which the clathrate hydrate dissociates into the clathrate host and liquid water: $M_pX_q.nH_2O(s) \rightarrow M_pX_q(g) + nH_2O(l)$, also represented as H = L + G or (hlg)

$\Delta H'_{diss}$ enthalpy change (in kJ·mol^{-1}) for the process in which the clathrate hydrate dissociates into the clathrate host and solid ice: $M_pX_q.nH_2O(s) \rightarrow M_pX_q(g) + nH_2O(s, ice)$, also represented as H = I + G or (hig)

$\Delta_f G^o(M_pX_q nH_2O, s)$/kJ mol^{-1} standard Gibbs energy of formation (in kJ·mol^{-1}) of the clathrate hydrate $M_pX_q.nH_2O$

$S^o_{298}(M_pX_q.nH_2O, s)$ /J K^{-1} mol^{-1} standard entropy (in J·K^{-1}·mol^{-1}) of the clathrate hydrate $M_pX_q.nH_2O$

$\Delta P(M_pX_q nH_2O, s)$ general thermodynamic property, P, of the clathrate hydrate $M_pX_q.nH_2O$. P can be $\Delta_f G^o$, $\Delta_f H^o$, S^o_{298} etc.

$\Theta_{Hf}(H_2O, s-g)$ proportionality constant (in kJ mol^{-1}) relating the standard thermodynamic enthalpy of formation, $\Delta_f H^o$ of the gas hydrate to n.s–g signifies that the gas hydrate is a solid (s) *e.g.* $CO_2.10H_2O$ (s) and the clathrate host is in gaseous form (g) *e.g.* $CO_2(g)$

(anhydrous) compound of formula M_pX_q for which $n = 0$ Water forms gas (clathrate) hydrates [10] when water is frozen in the presence of gaseous Ar, Kr, Cl_2, SO_2, CO_2, CH_3Cl *etc.*; the gaseous CH_4 hydrate occurs naturally. In the case of SO_2, CO_2, CH_3Cl and CH_4 the standard enthalpies of formation are not zero since the gases do not represent their standard states and so Eq. (1) no longer applies in these cases. These gases when combined to form clathrate hydrates are of more commercial interest than those treated in Part 1 and access to thermodynamic data for these via the equations produced in this current paper will provide easy and quick access to such data not previously available.

1.1.1. The thermodynamic Difference Rule (TDR) for inorganic gas hydrates

In its standard form TDR is represented by the equation:

$$[\Delta P(M_pX_q.nH_2O, s) - \Delta P(M_pX_q, s)] = n\Theta_P(H_2O, s-s) \quad (2)$$

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

For a gas clathrate hydrate, when considering standard enthalpies of formation, $\Delta_f H^o$ where the parent is in the gaseous state, Eq. (2) will take the specific form:

$$[\Delta_f H^o(M_pX_q.nH_2O, s) - \Delta_f H^o(M_pX_q, s)]/kJmol^{-1}$$
$$= n\Theta_{Hf}(H_2O, s-g) \quad (3)$$

The function on the left hand side of Eq. (3) and enclosed in square brackets, is called the Difference Function which, when plotted versus n, should give a rectilinear graph which passes through the origin and whose gradient is $\Theta_{Hf}(H_2O, s-g)$, see Fig. 1. The correlation coefficient, R^2 is very close to unity ($R^2 = 0.9998$)
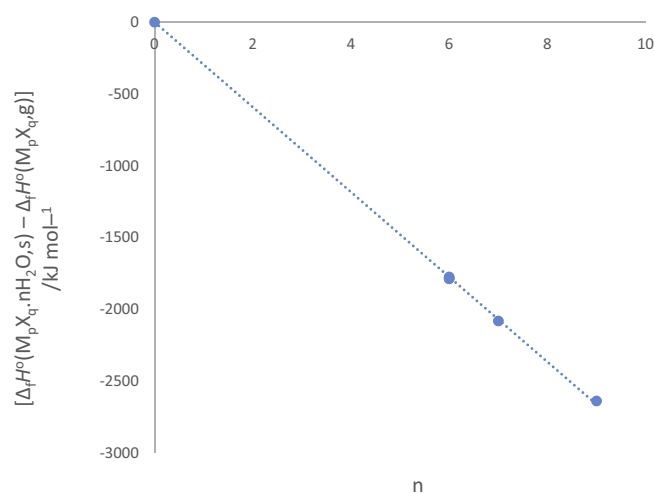

Fig. 1. Difference function plotted as ordinate versus n. Gradient = $\Theta_{Hf}(H_2O, s-g)$.

1.1.2. Enthalpies of dissociation of clathrate hydrates

Two types of dissociation process are usually considered when discussing clathrate hydrates and it is for these two processes that experimental data are normally sought. These quantities are almost always determined by use of the Claperyron equation [13]. The first process, denoted [14–17] by H = L + G or (hlg) and ΔH_{diss} is:

$$M_pX_q.nH_2O(s) \rightarrow nH_2O(l) + M_pX_q(g) \quad (4)$$
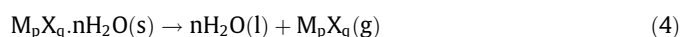
for which at 298 K and 1 atm pressure we can write:

$$\Delta H_{diss} = \Delta_f H^o(M_pX_q, g) + n\Delta_f H^o(H_2O, l)$$
$$- \Delta_f H^o(M_pX_q.nH_2O, s)$$
$$= [\Delta_f H^o(M_pX_q, g) - \Delta_f H^o(M_pX_q.nH_2O, s)] - 285.8n \quad (5)$$

using $\Delta_f H^o(H_2O, l)$/kJ mol^{-1} = −285.8 [18].

The second dissociation process, denoted [14–17] by H = I + G or (hig) and $\Delta H'_{diss}$ is:

$$M_pX_q.nH_2O(s) \rightarrow nH_2O(s, ice) + M_pX_q(g) \quad (6)$$