



# A simplification of gas clathrate hydrate thermochemistry using the Thermodynamic Difference Rule (TDR). Part 4. Further extension of the TDR to temperatures other than 298 K and validation of the similarity found between inorganic hydrate and clathrate hydrate TDR equations

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## ABSTRACT

This paper continues the investigation of the role of TDR equations as they apply to heat capacity data. A TDR equation is proposed and investigated using heat capacity data for  $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_6 \cdot 7.67\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_8 \cdot 17.0\text{H}_2\text{O}$ ,  $\text{Xe} \cdot 5.90\text{H}_2\text{O}$ ,  $\text{Xe} \cdot 6.29\text{H}_2\text{O}$  and  $\text{Kr} \cdot 6.10\text{H}_2\text{O}$ . Variation of  $\Theta_{C_p}(\text{H}_2\text{O}, s - g)/\text{J K}^{-1} \text{mol}^{-1}$  is examined as a function of temperature,  $T/\text{K}$  by fitting a linear regression line. The main conclusion of the paper is that the equation:

$$[C_p(\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}, s, T) - C_p(\text{M}_p\text{X}_q, g, T)] = [0.1378T/\text{K} + 0.7972]n$$

represents a TDR equation capable of yielding an estimate of heat capacity,  $C_p(\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}, s, T)$  for any general hydrate (gas hydrate or conventional inorganic hydrate) in the temperature,  $T/\text{K}$ , range 100–300 K, with errors not usually greater than 10% and often considerably less than this.

So vast are the capabilities of the TDR that a proposal is made for the creation of a vast database of entirely self-consistent thermodynamic data for hydrates and their parents without use of further experimental calorimetry.

The TDR is used to determine an improved value for the heat capacity of the tetrahydrate of beryllium sulfate:

$$C_p(\text{BeSO}_4 \cdot 4\text{H}_2\text{O}, s)/\text{J K}^{-1} \text{mol}^{-1} = 247.1.$$

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## 1. Introduction

Under standard conditions at 298 K and for conventional inorganic hydrates the Thermodynamic Difference Rule (TDR) [1–11] takes the simple general form:

$$[P(\text{M}_p\text{X}_q \cdot n\text{H}_2\text{O}, s) - P(\text{M}_p\text{X}_q, g)] = n\Theta_p(\text{H}_2\text{O}, s - s) \quad (1)$$

where  $P$  is any standard thermodynamic property, which can be  $\Delta_f H^\circ$ ,  $\Delta_f G^\circ$ ,  $S_{298}^\circ$ ,  $C_p^\circ$  etc,  $n$  is the number of water molecules per formula unit of the hydrate and  $\Theta_p(\text{H}_2\text{O}, s - s)$  is a constant ( $= -299 \text{ kJ mol}^{-1}$  when  $P = \Delta_f H^\circ$ ;  $-242 \text{ kJ mol}^{-1}$  when  $P = \Delta_f G^\circ$ ;  $41 \text{ J K}^{-1} \text{mol}^{-1}$  when  $P = S_{298}^\circ$  and also when  $P = C_p^\circ$ ). In Part 1 [1] I dealt with gaseous clathrate hydrates for which the parent gaseous

molecule was in its standard reference state at 298 K and 101 kPa pressure,  $\Delta_f H^\circ(\text{M}_p\text{X}_q, s)/\text{kJ mol}^{-1} = 0$  e.g.  $\text{Xe} \cdot 6\text{H}_2\text{O}$ . Here the available experimental data for  $\Delta_f H^\circ$  fitted the above equation well and moreover the value of  $\Theta_p(\text{H}_2\text{O}, s - g)$ ,  $P = \Delta_f H^\circ$  was very close in magnitude to that of  $\Theta_p(\text{H}_2\text{O}, s - s)$ ,  $P = \Delta_f H^\circ$  found for the inorganic solid hydrates (see reference [5], Table 1, column 6). Part 2 [2] dealt with  $\Delta_f H^\circ$  for more commercially important gas clathrate hydrates, e.g.  $\text{CH}_4 \cdot 6.07\text{H}_2\text{O}$  where a similar TDR equation was found to be valid at 298 K. In this case the gaseous molecule concerned is no longer in its standard state (i.e.  $\Delta_f H^\circ(\text{M}_p\text{X}_q, s)/\text{kJ mol}^{-1} \neq 0$ ). These equations predicted results for the thermodynamic parameters that mirrored the experimental data extremely closely.

The findings, thus far, suggested that the TDR equations developed from the classic inorganic hydrates had constants which

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### Nomenclature

$M_pX_q$  general formula for the gas or **n** liquid clathrate host.  
e.g. Ar, Kr, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>

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

$P(M_pX_q \cdot nH_2O, s)$  standard thermodynamic property,  $P$  where  $P$  can be  $\Delta_f H^\circ$ ,  $\Delta_f G^\circ$ ,  $S_{298}^\circ$  and  $C_p$

$C_p(M_pX_q \cdot nH_2O, s)$  heat capacity (in  $J K^{-1} mol^{-1}$ ) of the clathrate hydrate  $M_pX_q \cdot nH_2O$

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

$S_{298}^\circ(M_pX_q \cdot nH_2O, s)$  standard entropy (in  $J K^{-1} mol^{-1}$ ) of the clathrate hydrate  $M_pX_q \cdot nH_2O$ .

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

$\Theta_{Cp}(H_2O, s - g)$  proportionality constant (in  $J K^{-1} mol^{-1}$ ) relating the heat capacity of the gas hydrate to  $n$ .  $s - g$  signifies that the gas hydrate is a solid (s) e.g.  $N_2 \cdot 6.28H_2O$  (s) and the clathrate host is in gaseous form (g) e.g.  $N_2(g)$

$\Theta_{Cp}(H_2O, s - g, TK)$  value of  $\Theta_{Cp}(H_2O, s - g)$  at temperature,  $T/K$

would be equally valid (or nearly so) for the gaseous clathrate hydrates. Thus, even in the complete absence of data for  $\Delta_f G^\circ$  and  $S_{298}^\circ$  for the clathrate hydrates we were able to conjecture a likely form of TDR equation to use to estimate these parameters at 298 K coupled with the extreme likelihood that they would predict experimental values which were extremely close to reality.

In Part 3 [3] we conjectured further that a TDR equation for heat capacity,  $C_p$ , of the gaseous clathrate hydrate ought to adopt a similar form to that previously found for solid inorganic hydrates. Although the heat capacity data examined in this paper was invariably based on extrapolated data – sometimes extrapolated by a considerable increment – nevertheless the predicted and experimental heat capacities once again agree extremely well. The  $\Theta_{Cp}(H_2O, s - g)$  value emerging being, again, close to the inorganic hydrate value,  $\Theta_{Cp}(H_2O, s - s)$ .

If we knew how the parameters of the TDR equation above when  $P = C_p$  varied with temperature we could then test TDR predictions for values of  $C_p$  actually within the Handa temperature ranges [12–14] and thus avoid the need to deal with extrapolated values. This is the subject of this present paper. What emerges is that the speculations made concerning similarity found between inorganic hydrate and clathrate hydrate parameters appear to be totally correct and TDR once again emerges as a *force majeure* for the prediction of missing thermodynamic data not only at 298 K but at other temperatures too.

Incredibly it does appear that the TDR approach could be exploited as a major means of estimating standard thermodynamic data when either experimental methods are unavailable or just not feasible. In cases also where data for the “parent” compound,  $M_pX_q$ , is sought then knowledge of the appropriate thermodynamic data for just ONE of its hydrates would be sufficient to determine its value. This will be the subject of Part 5 and subsequent papers in this series.

## 2. TDR equations at 298.15 K and at other temperatures

On the basis of my studies on the solid inorganic hydrates [1–11] one would suppose an equation such as:

$$[C_p^\circ(M_pX_q \cdot nH_2O, s) - C_p^\circ(M_pX_q, g)]/J K^{-1} mol^{-1} = n\Theta_{Cp}(H_2O, s - s) = 42.8n \quad (2)$$

would possibly work quite well for the clathrate hydrates.

### 2.1. Methane clathrate hydrate, $CH_4 \cdot 6.00H_2O$

Fortunately data exist for us to test this idea. In Table 1, heat capacity data at three different temperatures is assembled from various literature sources. Using the data from Table 2, the “Difference Function” (which corresponds to the left hand side of Eq. (2)) is evaluated. At each temperature there is a single value of this function because data for only a single value of  $n$  is available.

The gradient,  $\Theta_{Cp}(H_2O, s - g)/J K^{-1} mol^{-1}$  of the Difference Plot is, in the case where we have knowledge of  $C_p$  for only a single value of  $n$ , calculated using the equation:

$$\Theta_{Cp}(H_2O, s - g)/J K^{-1} mol^{-1} = [C_p(M_pX_q \cdot nH_2O, s) - C_p(M_pX_q, g)]/n \quad (3)$$

The value at (100, 200 and 298.15) K obtained appears in column 3 of Table 2 and a typical plot for methane hydrate is displayed in Fig. 1.

From the results from Table 2 emerge TDR equations applicable to each of  $t$  temperatures considered:

$$[C_p(CH_4 \cdot 6.00H_2O, s) - C_p(CH_4, g)]/J K^{-1} mol^{-1} = n\Theta_{Cp}(H_2O, s - g, 100 K) = 14.7n \quad (4)$$

**Table 1**  
Heat capacity for methane gas and for the clathrate hydrate,  $CH_4 \cdot 6.00H_2O$ , at 100 K, 200 K and 298.15 K.

$T$	$C_p(CH_4, g)/J K^{-1} mol^{-1}$			$T/K$	$C_p(CH_4 \cdot 6.00H_2O, s)/J K^{-1} mol^{-1}$	
	Barin [15]	NIST [16]	Technical Note 270–3 [17]		Table 3 Handa [12]	Eq. (3) Table 4 Handa [12]
100		33.28 <sup>a</sup>		100	121.4	
200		33.5 <sup>a</sup>		200	201.4	
298.15	35.645	35.69 <sup>a</sup>	35.31	298.15		(283.8) <sup>b</sup>

<sup>a</sup> Value taken from NIST webbook [16].

<sup>b</sup> Estimated value at 298.15 K using equation coefficients in Table 4 of Ref. [12]:  $C_p(CH_4 \cdot 6H_2O, s)/J K^{-1} mol^{-1} = 6.6 + 1.4538 T/K - 0.3640 \times 10^{-2} (T/K)^2 + 0.6312 \times 10^{-5} (T/K)^3$  (N.B. The empirical equation holds for temperatures in the range 85 K to 270 K, hence the value recorded is an extrapolated one at 298.15 K).

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