

## Letters

## Campbell's Rule for Estimating Entropy Changes

## Refining Campbell's Rule

In a recent article (1), Norman Craig has proposed the rule-of-thumb that the approximate value of the entropy of reaction ( $\Delta_r S^\circ$ ) is related to the net moles ( $\Delta n_g$ ) of gas consumed or generated in the reaction by the relation:

$$\Delta_r S^\circ / [J(K \text{ mol rxn})^{-1}] \approx 140 \Delta n_g / \text{mol} \quad (1)$$

The numerical constant in this approximation was obtained by averaging the values of  $\Delta_r S^\circ / \Delta n_g$  calculated for ten of the eleven example reactions (excluding the one for which  $\Delta n_g = 0$ ) given in Table 1 of Craig's paper (1), and then combining this with the average of the values of  $\Delta_r S^\circ / \Delta n_g$  for 18 of the 23 reactions given in Tables 1 and 2 of an earlier paper by Campbell (again excluding the cases where  $\Delta n_g = 0$ ) (2). The average for Craig's data was 148 J (K mol rxn)<sup>-1</sup>(mol)<sup>-1</sup>, whereas that for Campbell's data was 136 J (K mol rxn)<sup>-1</sup>(mol)<sup>-1</sup>, with a combined average of 140 J (K mol rxn)<sup>-1</sup>(mol)<sup>-1</sup>, as given in the approximation in eq 1.

If, instead of following the above procedure, one plots the values of  $\Delta_r S^\circ$  versus  $\Delta n_g$  (including those for which  $\Delta n_g = 0$ ) for each data set, and uses a least squares analysis to obtain the best straight line fit, one obtains the results (rounded to the nearest tenth) summarized in Table 1, where those for Craig's eleven examples are given in the first row; those for Campbell's 23 examples<sup>1</sup> are given in the second row; and those for the combined Craig–Campbell data sets are given in the third row. If one evaluates the correlation equation for Craig's data (row 1) at  $\Delta n_g = 1$ , one obtains a value of 149.8 J (K mol rxn)<sup>-1</sup>, which is essentially identical to Craig's reported average of 148 J (K mol rxn)<sup>-1</sup>(mol)<sup>-1</sup>. If, however, one does the same for Campbell's data set (row 2), one obtains a value of 120.9 (K mol rxn)<sup>-1</sup> at  $\Delta n_g = 1$ , which is substantially lower than the value of 136 J (K mol rxn)<sup>-1</sup>(mol)<sup>-1</sup> reported by Craig. This discrepancy is apparently due to the fact that we have included the  $\Delta n_g = 0$  cases eliminated by Craig. Because of this discrepancy, a similar divergence is obtained for the case of the combined data sets (row 3), where  $\Delta n_g = 1$  gives an average value of 128 J (K mol rxn)<sup>-1</sup> rather than the value of 140 J (K mol rxn)<sup>-1</sup>(mol)<sup>-1</sup> reported by

Craig. Since the intercept of the correlation equation for the combined case is so small (−0.8 J (K mol rxn)<sup>-1</sup>), the full equation may be approximated by the simpler relation:

$$\Delta_r S^\circ / [J(K \text{ mol rxn})^{-1}] \approx 128 \Delta n_g / \text{mol} \quad (2)$$

which gives a more statistically significant result than does the approximation in eq 1.

The question naturally arises as to why the average for Campbell's data set is so much lower than that for Craig's data set. In this regard, it is of interest to note that only 6 out of 23, or about 26%, of Campbell's examples involve solids or liquids as well as gases, whereas 9 out of 11, or about 82%, of Craig's examples do. In other words, most of Campbell's examples involve only the compensation of  $\Delta n_g$  terms, whereas many of Craig's examples involve the additional compensation of  $\Delta n_s$  and  $\Delta n_l$  terms as well. Likewise, 7 out of 23, or about 30%, of Campbell's examples involve H<sub>2</sub>(g) or H(g), whereas only 2 out of 11, or about 18%, of Craig's examples do. The relevance of this latter observation has to do with the well-known logarithmic dependence of the entropy of translation ( $\Delta_{tr} S^\circ$ ) of gases on their molecular weights (MW), as given by the Sackur–Tetrode equation (3):

$$\Delta_{tr} S^\circ / [J(K \text{ mol})^{-1}] \approx 109 + 28.7 \log(\text{MW}) \quad (3)$$

(at 298 K)

As Craig emphasizes, Campbell's rule is based on the fact that  $\Delta_r S^\circ$  is dominated by the  $\Delta_{tr} S^\circ$  values of the gaseous species and this logarithmic dependency means, in turn, that  $\Delta_{tr} S^\circ$  varies more rapidly for gases of low molecular weight, such as H<sub>2</sub> and H, than it does for gases of higher molecular weight,<sup>2</sup> as may be seen from Figure 4.4 of ref 3.

## Notes

1. This correlation incorporates the corrected entropy values given by Craig in footnote 2 of his paper (1).
2. Interestingly, the weighted average of the molecular weights of all of the gaseous species appearing in Craig's examples is 30.9, which gives a value of  $\Delta_{tr} S^\circ = 151.8$  J (K mol)<sup>-1</sup> when substituted into the Sackur–Tetrode equation. This is a reasonable approximation to the average value of 149.8 J (K mol rxn)<sup>-1</sup> for  $\Delta_r S^\circ$  reported for this data set. Unfortunately, no such similar agreement is obtained with Campbell's data set.

## Literature Cited

1. Craig, N. C. *J. Chem. Educ.* **2003**, *80*, 1432–1436.
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3. Dascent, W. E. *Inorganic Energetics*, 2nd ed.; Cambridge University Press: Cambridge, 1982; pp 137–138.

## William B. Jensen

Department of Chemistry  
University of Cincinnati  
Cincinnati, OH 45221-0172

Table 1. Correlation of  $\Delta_r S^\circ$  and  $\Delta n_g$

Data Set	N	Correlation Equation	R	$\Delta_r S^\circ / J(K \text{ mol rxn})^{-1}$ at $\Delta n_g = 1$
Craig	11	$\Delta_r S^\circ = 19.2 + 130.6 \Delta n_g$	0.99	149.8
Campbell	23	$\Delta_r S^\circ = -9.6 + 130.5 \Delta n_g$	0.96	120.9
Combined	34	$\Delta_r S^\circ = -0.8 + 128.8 \Delta n_g$	0.98	128

## Letters

The author replies:

Regarding Campbell's Rule

I am pleased that Campbell's rule for estimating entropy changes in gas-consuming and gas-producing chemical reactions (1) has attracted immediate interest (2). William Jensen's graphical analysis has uncovered an aspect of selecting a numerical value for Campbell's rule that was overlooked in the original presentation. A revised value for Campbell's rule is  $\Delta_r S^\circ/\Delta n_g = 130 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$ .

With the exception of the cases for which  $\Delta n_g = 0$  in both Tables 1 and 2 of Campbell's paper (3), the unremarked omission of the Trouton's rule value in Table 1 (3), and the unremarked correction in the first entry of Table 2 (3), for which  $\Delta_r S^\circ = 64 \text{ J (K mol rxn)}^{-1}$  for  $\Delta n_g = 0.5$ , the remaining 18 values from Tables 1 and 2 were incorporated in computing the reported average of  $136 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$ . Unfortunately, some errors crept into Table 1 in ref 1. The corrections are:

$\Delta_r S^\circ = 181.8 \text{ J (K mol rxn)}^{-1}$  and an unchanged ratio for  $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ ;

a ratio of  $136 \text{ J (K mol rxn)}^{-1}$  for  $\text{Fe}(\text{c}) + 5\text{CO}(\text{g}) \rightarrow \text{Fe}(\text{CO})_5(\text{l})$ ;

and  $\Delta_r S^\circ = 108.3 \text{ J (K mol rxn)}^{-1}$  for  $\text{HgO}(\text{c}) \rightarrow \text{Hg}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$  and a corresponding ratio of  $217 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$ .

The average ratio for the data in Table 1 (1) becomes  $149 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$ . With these revisions and three revised values from the two tables in Campbell's paper, the straight line fit to all the data, including reactions for which  $\Delta n_g = 0$ , becomes  $\Delta_r S^\circ = 1.9 + 130.1\Delta n_g$  ( $R = 0.98$ ). This result gives an estimate of the Campbell's rule value of  $132 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$ , which is the same as the value derived recently from ab initio calculations of molecular properties by Watson and Eisenstein for reactions of gases only (4).

The cause of the discrepancy between the average value of about  $140 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$  reported in ref 1 and

Jensen's value found from fitting a straight line is an overlooked consequence of the averaging process. In the averaging process all of the data were taken as positive. If the same data as used for the fit given above, but made positive, are fit to a straight line, the result is  $\Delta_r S^\circ = 16.8 + 121.3\Delta n_g$  ( $R = 0.96$ ), which is, of course, comparable to averaging to obtain a value of about  $140 \text{ J (K mol rxn)}^{-1} \text{ mol}^{-1}$  reported in ref 1. The big discrepancy arises from the unexpectedly large intercept value of 16.8. Jensen makes a similar observation. When negative values as well as positive values are used in the fitting, a reasonable intercept near zero for  $\Delta n_g = 0$  is obtained.

Because Campbell's rule is numerically approximate with an uncertainty range of about  $\pm 40\%$  (23% statistical average), we must be careful not to put a fine point on its value. The numerical value depends on the choice of reactions used in illustrating the rule. In Campbell's tables (3), species are gases with few exceptions, but the stoichiometry varies. In Table 1 in ref 1, a more varied set of reactions involving solids and liquids along with different stoichiometries is given. Of course, a great number of reactions could be considered to obtain a statistically "more significant" value for the rule. In addition, as Jensen points out, the participation of exceptionally light  $\text{H}_2(\text{g})$  or  $\text{H}(\text{g})$  in a reaction makes significant differences in  $\Delta_r S^\circ$ . In view of these complications, the selection of a value for Campbell's rule rests on judgment as much as on statistics.

#### Literature Cited

1. Craig, N. C. *J. Chem. Educ.* **2003**, *80*, 1432–1436.
2. Jensen, W. B. *J. Chem. Educ.* **2004**, *81*, 1570.
3. Campbell, J. A. *J. Chem. Educ.* **1985**, *62*, 231.
4. Watson, L. A.; Eisenstein, O. *J. Chem. Educ.* **2002**, *79*, 1269–1277.

#### Norman C. Craig

Department of Chemistry  
Oberlin College  
Oberlin, OH 44074