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Comments

Simplification of Thermodynamic Calculations Through Dimensionless Entropies

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We have been discussing with our colleagues at various meetings this past year the advantages of using dimensionless entropies to simplify thermodynamic calculations. The response has been very favorable and we are endeavoring to acquaint a larger group to these advantages through publication of these comments in journals that emphasize thermodynamics such as *High Temperature Science* and the *Journal of Physical and Chemical Reference Data*.

Where dimensionless quantities determine the behavior of physical systems, there are many advantages in tabulating data in the form either of these same dimensionless quantities or of quantities as closely related thereto as feasible. There are opportunities in chemical thermodynamics and statistical mechanics to simplify calculations and to increase understanding by changes of this sort. In particular the thermodynamic behavior is determined by the interplay of two factors, each dimensionless. First is the *a priori* probability of various states while the second category comprises the ratios of energy differences to thermal energy at the temperature of interest. The probability ratios (W_j/W_i) are dimensionless and take on dimensions only when expressed as entropies by the relationship.

$$\Delta S = R \ln(W_j/W_i).$$

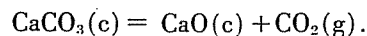
We shall see that there are practical as well as conceptual advantages in the use of the dimensionless form (S/R) in tabulating entropy data.

Energies are measured by many types of experiments and much interconversion of units is necessary. But for use in chemical thermodynamics one eventually wants the dimensionless ratio to thermal energy given by expressions such as

$$\ln K = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (1)$$

Thus if energies and enthalpies are divided to R to yield (H/R), (G/R), etc., one has quantities of the dimension temperature and the unit kelvin which can be divided by the temperature of interest to obtain the desired results. By working with and tabulating energies in kelvins, their significance at a given temperature becomes obvious. Otherwise a calculation introducing R in the appropriate units is necessary.

As an example let us consider the dissociation of calcite



On this new basis the relevant thermodynamic properties at 298.15 K are given in table 1. From these data one calculates $\Delta(S^\circ/R) = 19.13$ and $\Delta(H^\circ/R) = 21450$ K at 298.15 K. For this reaction $K = f_{\text{CO}_2} = P_{\text{CO}_2}$ at low pressure. One may at once estimate the temperature at which the dissociation pressure is unity ($\ln K = 0$) as

$$T \cong \frac{\Delta(H^\circ/R)}{\Delta(S^\circ/R)} \cong \frac{21450}{19.13} \cong 1120 \text{ K}.$$

This estimate assumes, of course, that ΔC_p° is zero whereupon ΔS° and ΔH° are independent of temperature. But ΔC_p° , although small in this case, is not zero.

The most convenient method for an exact calculation is the use of the function $-(G^\circ - H^\circ_{298})/RT$ which has been commonly tabulated in this form without the R or in other forms closely related thereto. On the new basis one has the data in table 2. From these values one calculated $-\Delta(G^\circ - H^\circ_{298})/RT$ for the reaction and then obtains the equilibrium constant from the equation.

$$\ln K = -\Delta \left(\frac{G^\circ - H^\circ_{298}}{RT} \right) - \frac{\Delta(H^\circ_{298}/R)}{T}. \quad (2)$$

These quantities are given in table 3.

The temperature at which the dissociation pressure is unity can be accurately calculated using the $-\Delta(G^\circ - H^\circ_{298})/RT$ values from table 3 with little more effort than the previous approximate calculation using $\Delta(S^\circ/R)$.

TABLE 1. Thermodynamic properties at 298.15 K

	$\left(\frac{\Delta H_f^\circ}{R}\right)/K$	$\left(\frac{\Delta G_f^\circ}{R}\right)/K$	$\left(\frac{S^\circ}{R}\right)$	$\left(\frac{C_p^\circ}{R}\right)$	Ref.
CO ₂ (g)	- 47 330	- 47 437	25.701	4.466	1
CaO(c)	- 76 385	- 72 650	4.596	5.066	2
CaCO ₃ (c) (calcite)	-145 160	-135 770	11.17	9.85	3

TABLE 2. Values of $-(G^\circ - H_{298}^\circ)/RT$

	900	1000	1100	1200	Ref.
CO ₂ (g)	27.952	28.362	28.76	29.135	1
CaO(c)	7.079	7.513	7.93	8.32	2
CaCO ₃ (c) (calcite)	16.40	17.35	18.26	19.13	3, 4

TABLE 3. Values for equation 2

T/K	$-\Delta\left(\frac{G^\circ - H_{298}^\circ}{RT}\right)$	$-\Delta\left(\frac{H_{298}^\circ/R}{T}\right)$	$\ln f_{CO_2}$
900	18.63	-23.83	-5.20
1000	18.53	-21.45	-2.82
1100	18.43	-19.50	-1.07
1200	18.33	-17.87	+0.46

Thus

$$T = \frac{\Delta H_{298}^\circ/R}{-\Delta(G^\circ - H_{298}^\circ)/RT}$$

yields $T > 1164$ K using the value of $-\Delta(G^\circ - H_{298}^\circ)/RT = 18.43$ for 1100 K and $T < 1170$ K using the value of $-\Delta(G^\circ - H_{298}^\circ)/RT = 18.33$ for 1200 K and $T = 1168$ K using the interpolated value of 18.36. The function $-\Delta(G^\circ - H_{298}^\circ)/RT$ can be thought of as $\Delta S^\circ/R$ corrected for the contribution of $\Delta C_p^\circ/R$ when used with $\Delta H_{298}^\circ/R$ for calculation over the entire temperature range.

It is apparent that $-\Delta(G^\circ - H_{298}^\circ)/RT$ varies only slowly with temperature; hence it is easily interpolated. Correspondingly a plot of $\ln K$ vs $1/T$ is nearly linear. All of these results are, of course, well-known and the conventional calculations in the past have differed only in the use of quantities larger by the factor $R = 1.987$ cal K⁻¹ mol⁻¹ until the final step which constituted a division by R to obtain $\ln K$ (or by $2.303 R$ to obtain $\log K$). Since we now use calculators which yield natural logarithms or exponentials most conveniently, it is a small but significant simplification to use the quantities divided by R and avoid one step in the calculation.

This apparently small simplification becomes much more important, however, when one recognizes the current interest in replacing the calorie by the joule as the unit of

energy. If we were to have a period in which the working tables of data were partly in calories and partly in joules, there would be much inconvenience and opportunity for error. All of these problems can be avoided by the alternative here proposed where all quantities are either dimensionless or of dimension temperature and unit kelvin.

A few historical remarks are appropriate at this point. Originally, thermochemical measurements were made in terms of the temperature change of a measured amount of water and were accordingly reported in calories (the heat to warm one gram of water by one degree at the temperature of the experiment). Later, when more precise measurements related chemical energy effects to electrical energy, the calorie was retained as a defined unit with one thermochemical calorie equal to 4.1833 Int. joules. The electrical measurements of that period (until 1948) were made in terms of empirically compared International volts, amperes, and ohms which were near but not exactly equal to the corresponding absolute units. After 1948 electrical measurements were made in absolute electrical units and the corresponding change was made in the definition of the thermochemical calories to 4.1840 abs joules. While the use of joules instead of calories has been suggested repeatedly, there were serious objections when confusion between International and absolute joules was likely. Also the simplicity for rough calculations of the value $R = 1.987 \approx 2.0$ cal K⁻¹ mol⁻¹ as compared to $R = 8.314$ J K⁻¹ mol⁻¹ tended to perpetuate the use of calories. But by following the procedures here suggested one will use the numerical value of R only infrequently. Thus there will be no need for future use of the calorie, although the past literature will require the reader to be able to work with that unit.

When data in the literature have been obtained from statistical mechanical calculations and then multiplied by R it is necessary, of course, to divide by the same value of R used by the author. For other data, the values of R given in table 4, which are the most accurate values known to-date, would be used. When dimensioned values are desired of energies in joules, calories, cm⁻¹, Btu or other units, or of cell potentials in volts, they are readily obtained by multiplication by the appropriate value of R or other factor. Several such values are given in table 4.

TABLE 4. Physical constants (Refs. 5,6)

$$R = 8.3144 \pm 0.0003 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 1.98719 \pm 0.0008 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\frac{R}{F} = (8.6172 \pm 0.0003) \times 10^{-5} \text{ V K}^{-1}$$

$$\frac{k}{hc} = 0.69503 \pm 0.00002 \text{ cm}^{-1} \text{ K}^{-1}$$

$$F = 96486.5 \pm 0.3 \text{ J V}^{-1} \text{ or } 23060.8 \pm 0.1 \text{ cal V}^{-1}$$

$$N_A = (6.022094 \pm 0.000006) \times 10^{23} \text{ mol}^{-1}$$

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