Letters

Reaction Feasibility and the Planck Function

I welcome the recent article by Rosenberg and Klotz ([1]) summarizing the advantages of using the Planck function (Y) as an alternative to the Gibbs free-energy function (G) in discussing chemical equilibrium. I have used a slight modification of the Planck function in my classes for the last 20 years. I call this modification the "reaction feasibility" function ($\mathscr{F}$). It is defined as

$$\mathscr{F} = -(\partial G/\partial \xi)/RT = -\Delta H°/RT + \Delta S°/R - \ln Q = \mathscr{F}° - \ln Q \tag{1}$$

where ξ is the well-known extent of reaction parameter of De Donder ([2]) and Q is the activity quotient for the reaction in question at any given value of ξ:

$$Q = \prod_p a^\nu / \prod_r a^\nu \tag{2}$$

At equilibrium $\mathscr{F} = 0$. Consequently,

$$\mathscr{F}° = \ln Q_{eq} \quad \text{or} \quad Q_{eq} = e^{\mathscr{F}°} \tag{3}$$

where the equilibrium value of the activity quotient (Q_{eq}) is the same as the equilibrium constant K.

Obviously the reaction feasibility is related to the Planck function by the equation

$$\mathscr{F} = (\partial Y/\partial \xi)/R \tag{4}$$

In addition to the merits possessed by the Planck function, the reaction feasibility function has the further advantage of being a dimensionless number whose numerical value is independent of the units used to measure the component standard enthalpy and entropy changes (assuming, of course, that one divides by the appropriate value of the gas constant R).

The name "feasibility" was chosen to avoid the kinetic overtones inherent in the use of such terms as "spontaneous" and "spontaneity", which often suggest to the student the incorrect idea of an instantaneous, if not explosive, change. In applying the function, we are merely assessing whether the reaction in question is possible or feasible. If the answer is no ($\mathscr{F} < 0$), we need inquire no further. If the answer is yes ($\mathscr{F} > 0$), we then need to ask the further question of how fast the reaction will occur, which is, of course, a problem for chemical kinetics rather than thermodynamics. Describing a feasible but otherwise kinetically inert reaction as "spontaneous" obviously does violence to the everyday meaning commonly attached to this word.

One disadvantage of both the Planck function and the reaction feasibility function becomes apparent when one attempts to interface them with our current models of chemical kinetics. While it seems natural to think of a reaction as having to surmount an activation barrier, characterized by a free energy of activation, the alternative picture of the reaction as having to climb out of a "feasibility hole" is much less appealing and far less intuitive.

In passing, it should be noted that the reaction feasibility is also related to the De Donder affinity function (**A**) by the relation ([2, 3])

$$\mathscr{F} = \mathbf{A}/RT \tag{5}$$

Literature Cited

1. Rosenberg, R. M.; Klotz, I. M. *J. Chem. Educ.* **1999**, *76*, 1448.
2. De Donder, T.; van Rysselberghe, P. *Thermodynamic Theory of Affinity: A Book of Principles*; Stanford University Press: Stanford, CA, 1936.
3. Prigogine, I.; Dufay, R. *Chemical Thermodynamics*; Longmans, Green: London, 1954.

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