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Multidimensional thermochemical cycles – Exploring three dimensions: Designer tool for estimation of the thermodynamics of reactions under varying conditions and for estimating elusive thermodynamic data

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Dedicated to the memory of thes late Professor Manuel Ribeiro da Silva.

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ABSTRACT

Born–Haber–Fajans (BHF) thermochemical cycles describe links among different aspects of a chemical reaction at a common temperature and pressure, independent of the actual process of the reaction, and so provide methods for evaluation of otherwise missing information. We show that the standard two-dimensional BHF cycle can be extended to allow for consideration of temperature and pressure variation, using temperature changes for the reaction between HCl and Na as our illustrative example. Such extension provides possibilities of multiple interrelationships among contemplated states of the process of the reaction, so enhancing the related thermodynamic information.

Although thermodynamics and kinetics do not necessarily coincide, it may be possible, utilizing such insights, to circumvent kinetically-disallowed steps in a chemical synthesis by choosing an alternative but thermodynamically favored route.

1. Introduction

Most chemists are familiar with two-dimensional Born–Haber–Fajans cycles, which provide alternative routes by which the thermochemistry via the various key thermodynamic parameters ($\Delta_r H$, $\Delta_r S$, $\Delta_r G$, U_{POT} – where U_{POT} is the lattice potential energy) may be evaluated at fixed temperature and pressure, when the direct route may not be accessible. This is possible because these parameters are state functions [1], independent of the history of the system considered.

However, the standard limitation to two dimensions may readily be extended to multiple dimensions [2] by including variation in both temperature and pressure, which provides opportunities for deeper exploration of the interrelations of the thermodynamic parameters. We limit ourselves here to *three* dimensions in illustrating the concept, our purpose in this paper being to point out that, once constructed, such a cycle offers a ready means of identifying the multiple possible routes (and hence key interrelationships) between any given set of reactants and products and thereby a means of acquiring new thermodynamic data within the framework of a simple visible concept. This approach accords with increasing current practice in synthetic inorganic chemistry of including thermodynamic data and relating these data to other similar materials.

2. Three dimensional representations

Consider, for example, figure 1 in which two specific reactions are considered at three temperatures, *viz.* (170, 298, and 350) K, chosen to cover both the liquid and gaseous states of hydrochloric acid and chlorine, all at ambient pressure:

$$HCl(g) + Na(s) \rightarrow NaCl(s) + \frac{1}{2}H_2(g), \tag{1}$$

$$HCl(l) + Na(s) \rightarrow NaCl(s) + \frac{1}{2}H_2(g), \tag{2}$$

There are, needless to say, many other processes which can involve Na, H and Cl.

Since the enthalpy change for reaction (1) is a thermodynamic function of state, it is of course independent of the route taken between reactants and products. Thus, a whole series of thermodynamic relationships (equations (3)–(15) below) can be written, any one of which will enable the calculation of $\Delta_r H_{350}(1)$. It should be noted that these individual relations may not necessarily be

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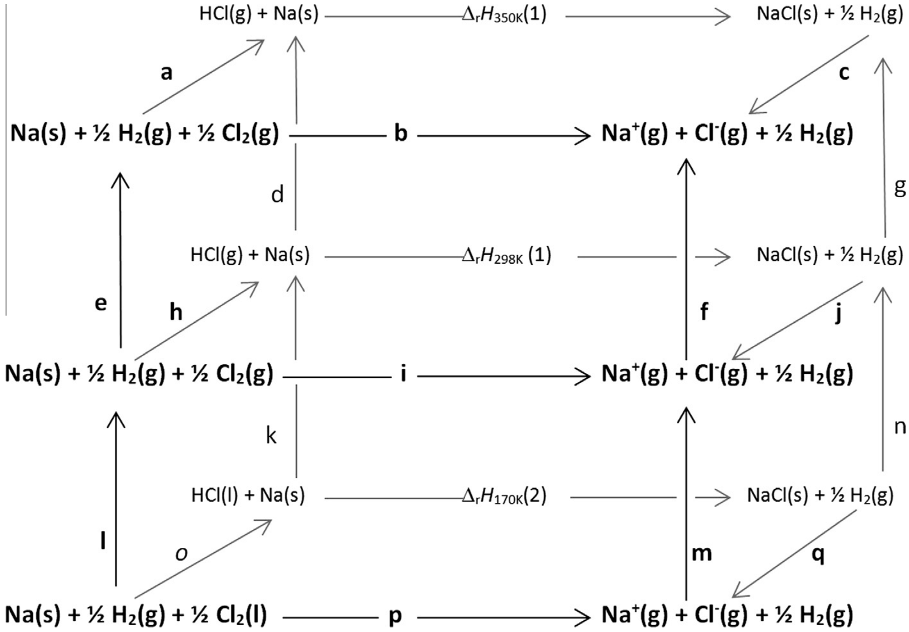

FIGURE 1. [2]: The three-dimensional thermochemical cycle based on reactions at temperatures (350, 298, and 170) K between HCl and Na, leading to the products NaCl and hydrogen gas (horizontal rear edges), the formation reactions at (350, 298, and 170) K of the reactants (horizontal left-hand side edges: *a*, *h*, *o*), the lattice potential energies at (350, 298, and 170) K (horizontal right-hand side edges: −*c*, −*j*, −*q*), the formation reactions at (350, 298, and 170) K of the gaseous Na^+ and Cl^- ions (horizontal front edges: *b*, *i*, *p*). Vertical edges *d*, *e*, *f*, *g*, *k*, *l*, *m*, *n* involve heat capacity terms required to raise the temperature of elements in their standard states (vertical, front, left hand side: *e*, *l*), gaseous ions and $H_2(g)$ (vertical, front, right-hand side: *f*, *m*), products (vertical, rear, right-hand side: *g*, *n*) and reactants (vertical, rear, left-hand side: *d*, *k*). Note the following [3]: HCl(g) condenses to become HCl(l) at *T* = 188 K, while $Cl_2(g)$ condenses to become $Cl_2(l)$ at *T* = 239 K.

straight-forward, and may themselves require to be evaluated by means of independent Born–Haber–Fajans cycles (cf. Supplementary Information). A number of thermodynamic parameters involved in the cycle have not been evaluated; these, *inter alia*, include: $[\Delta_f H_{350\,K}(Na^+,\ g) + \Delta_f H_{350\,K}(Cl^-,\ g)]$, $\Delta_r H_{170\,K}(2)$, $\Delta_{vap}H^o$ (HCl, l), $\Delta_f H_{170\,K}$(HCl, l) and $[\Delta_f H_{170\,K}(Na^+,\ g) + \Delta_f H_{170\,K}(Cl^-,\ g)]$.

2.1. Cycle relationships

Using the various routes possible between reactants and products at 350K we can write:

$$\Delta_r H_{350\ K}(1) = -\ a + b - c, \tag{3}$$

$$\Delta_r H_{350\ K}(1) = -\ \mathrm{d} + \Delta_r H_{298\ K}(1) + g, \tag{4}$$

$$\Delta_r H_{350\ K}(1) = -\ a - e + h + \Delta_r H_{298\ K}(1) + g, \tag{5}$$

$$\Delta_r H_{350\ K}(1) = -\ a - e + i - j + g, \tag{6}$$

$$\Delta_r H_{350\ K}(1) = -\ a - e - l + p - q + n + g, \tag{7}$$

$$\Delta_r H_{350\ K}(1) = -\ d - k + \Delta_r H_{170\ K}(2) + n + g, \tag{8}$$

$$\Delta_r H_{350\ K}(1) = -\ a + b - f - m - q + n + g, \tag{9}$$

$$\Delta_r H_{350\ K}(1) = -\ a + b - f - j + g, \tag{10}$$

$$\Delta_r H_{350\ K}(1) = -\ a - e + i + f - c, \tag{11}$$

$$\Delta_r H_{350\ K}(1) = -\ a - e - l + o + k + \Delta_r H_{298\ K}(1) + g, \tag{12}$$

$$\Delta_r H_{350\ K}(1) = -\ a - e - l + o + \Delta_r H_{170\ K}(2) + n + g, \tag{13}$$

$$\Delta_r H_{350\ K}(1) = -\ d - h - l + p - q + n + g, \tag{14}$$

$$\Delta_r H_{350\ K}(1) = -\ d - h + i - j + g. \tag{15}$$

The individual limbs can be linked to thermodynamic data as follows:

$$a = \Delta_f H_{350\ K}(\mathrm{HCl,g})/\mathrm{kJ \cdot mol^{-1}} = -92.4, \tag{16}$$

$$b = \Delta_f H_{350\ K}(\mathrm{Na^+,g}) + \Delta_f H_{350}(\mathrm{Cl^-,g}), \tag{17}$$

$$c = [U_{\mathrm{POT}}(\mathrm{NaCl}) - \mathrm{RT}]/\mathrm{kJ \cdot mol^{-1}} = U_{\mathrm{POT}}(\mathrm{NaCl}) - 2.91, \tag{18}$$

$$d = [C_p(\mathrm{HCl,g}) + C_p(\mathrm{Na,s})]\Delta T, \tag{19}$$

$$e = \left[\frac{1}{2}C_p(\mathrm{H_2,g}) + \frac{1}{2}C_p(\mathrm{Cl_2,g}) + C_p(\mathrm{Na,s})\right]\Delta T, \tag{20}$$

$$f = \left[C_p(\mathrm{Na^+,g}) + C_p(\mathrm{Cl^-,g}) + \frac{1}{2}C_p(\mathrm{H_2,g})\right]\Delta T, \tag{21}$$

$$g = \left[C_p(\mathrm{NaCl,s}) + \frac{1}{2}C_p(\mathrm{H_2,g})\right]\Delta T, \tag{22}$$

$$h = \Delta_f H^o(\mathrm{HCl,g}), \tag{23}$$

$$i = [\Delta_f H^o(\mathrm{Na^+,g}) + \Delta_f H^o(\mathrm{Cl^-,g})], \tag{24}$$

$$j = [U_{\mathrm{POT}}(\mathrm{NaCl}) - \mathrm{RT}], \tag{25}$$

$$k = C_p(\mathrm{HCl,l})\Delta T' + \Delta_{\mathrm{vap}}H^o(\mathrm{HCl,l}) + C_p(\mathrm{HCl,g})\Delta T'' + C_p(\mathrm{Na,s})\Delta T''', \tag{26}$$

$$l/(\mathrm{kJ \cdot mol^{-1}}) = \frac{1}{2}\Big[C_p(\mathrm{H_2,g})\Delta T'''' + C_p(\mathrm{Cl_2,l})\Delta T''''' + \Delta_{\mathrm{vap}}H^o(\mathrm{Cl_2,l}) + C_p(\mathrm{Cl_2,g})\Delta T''''''\Big], \tag{27}$$

$$m = \left[C_p(\mathrm{Na^+,g}) + C_p(\mathrm{Cl^-,g}) + \frac{1}{2}C_p(\mathrm{H_2,g})\right]\Delta T''', \tag{28}$$