The Extended Van't Hoff Equation & Its Significance

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Abstract: The well-known van't Hoff equation in chemical thermodynamics has been extended by making use of the van't Hoff isotherm, and the relationship between standard Gibbs energy of reaction $\Delta_r G^\circ$ and the total entropy change ΔS_{tot}. The resulting expression and its usefulness in studying the effect of temperature on the equilibria of exothermic and endothermic processes have been discussed in detail. The central role that the total entropy change plays in determining the dependence of equilibrium constant K_{eq} on temperature T has been emphasized.

Keywords: Van't Hoff Equation, Entropy, Exothermic, Endothermic, Haber - Bosch Process

1. Introduction

A very useful expression in chemistry to quantitatively determine the variation of equilibrium constant K_{eq} with temperature is the van't Hoff's law or the so-called van't Hoff's equation [1] commonly expressed as

$$ln \frac{K_{eq}(T_f)}{K_{eq}(T_i)} = \Delta_r H^\circ \left[\frac{1}{T_i} - \frac{1}{T_f} \right] \qquad (1)$$

The symbol $\Delta_r H^\circ$ refers to the standard enthalpy change of the reaction system under consideration and T_i and T_f, respectively, denote the temperatures at the beginning and end of the process. The standard state condition of the system is obtained by maintaining it under a constant pressure of 1 bar. In essence equation (1) says that knowing the value of equilibrium constant at one temperature one can determine its value at some other temperature provided one knows the value of standard enthalpy change of the reaction process under consideration [2–7]. The physical basis behind the variation of equilibrium constant with temperature is usually discussed in terms of the effect of T on the standard Gibbs energy change, $\Delta_r G^\circ$ of the reaction system [2]. The actual dependence of K_{eq} on temperature, that is its behavior when K_{eq} is plotted as a function of 1/T, depends on the sign of $\Delta_r H^\circ$ and the van't Hoff equation provides a theoretical basis of this dependence [2, 3].

No doubt such an analysis, based on the role of standard Gibbs energy of reaction, is a valid and accurate one to begin with it is, however, not the most general one. Recently, therefore, another related thermodynamical analysis of the problem that has gained ground [4] is in terms of the total entropy change ΔS_{tot}; more specifically $\Delta S_{tot} = \Delta S_{sur} + \Delta S_{sys} = -\Delta_r H^\circ/T + \Delta_r S^\circ$. Here ΔS_{sys} and ΔS_{sur}, respectively, denote the entropy changes of the system and surroundings, and $\Delta_r S^\circ$ denotes the standard entropy change of the reaction system under consideration. This later analysis, therefore, relies on the relative importance of the magnitudes of the entropy changes of the reaction system and its immediate surroundings. As per this viewpoint, when the reaction process is exothermic the term $-\Delta_r H^\circ/T$ contributes a positive entropy change to the surroundings, thus favoring the formation of product species. This contribution is fairly large at low temperatures. However, as the temperature of the reaction system is raised the magnitude of $-\Delta_r H^\circ/T$ term decreases. At higher temperatures, therefore, the extent of decrease may be such that the importance of the increasing entropy of the surroundings has a less significant role to play. As a consequence the equilibrium in such a case lies less towards the product side decreasing the value of equilibrium constant. In the case of an endothermic reaction the main contributing factor is the increase in entropy of the reaction system as a result of the energy as heat soaked up from the surroundings and the importance of the unfavourable entropy change of the surroundings $\Delta S_{surr} = -\Delta_r H^\circ/T$ gets reduced at higher temperatures and the reaction process shifts towards the product side as the temperature is increased, increasing the magnitude of equilibrium constant. This is a more fundamental origin of the behavior of equilibrium constant

towards temperature not the change in the value of $\Delta_r G^\circ$. The reason being that entropy is a fundamental property of the universe while free energy is a contrived or subsidiary property of the system [8]. Now because constraints on the use of change in the Gibbs free energy function, which is entropy change in disguise, affects its range of applicability [9], it is desirable to have a quantitative expression underlying the more fundamental explanation. It turns out that the van't Hoff equation can be extended and one can in that way obtain an alternative expression, similar to van't Hoff's yet quite different from it, underlying this most general explanation.

2. The Extended Van't Hoff Equation

A very well-known expression in chemical thermodynamics [10] is the relation between standard Gibbs energy of reaction $\Delta_r G^\circ$ and the total entropy change ΔS_{tot} :

$$\Delta_r G^\circ = -T\Delta S_{tot} \qquad (2)$$

ΔS_{tot} is sometimes also called $\Delta S_{universe}$ or $\Delta S_{isolated}$ but we won't use such designations here. For us the universe will consist of the system and its immediate surroundings as is usually the case in a typical chemistry laboratory [9, 11]. Another very important result from thermodynamics that we use here to extended the van't Hoff equation is the relation between equilibrium constant and standard reaction Gibbs energy or the so-called van't Hoff's isotherm:

$$\Delta_r G^\circ = -RT ln K_{eq} \qquad (3)$$

Comparison of equations (2) and (3) leads to the important expression:

$$\Delta S_{tot} = R ln K_{eq} \qquad (4)$$

Above result can also be rearranged into

$$K_{eq} = e^{\Delta S_{tot}/R} \qquad (5)$$

Although equation (5) does give some indication of the role that ΔS_{tot} plays in determining the behavior of equilibrium constant towards temperature it is useful to appreciate the role of ΔS_{tot} more fully. Furthermore, the full significance of equation (5) only becomes clear after one has extended the van't Hoff equation. To this end we first rewrite equation (1) in the form given below (using an important logarithmic law *lnab = lna – lnb* where *a* & *b* are constant numbers):

$$ln K_{eq}(T_f) - ln K_{eq}(T_i) = \Delta_r H^\circ \left[\frac{1}{T_i} - \frac{1}{T_f}\right]$$

Then we substitute equation (4) into the left hand side of above equation to yield:

$$\frac{\Delta S_{tot}(T_f)}{R} - \frac{\Delta S_{tot}(T_i)}{R} = \frac{\Delta_r H^\circ}{R}\left[\frac{1}{T_i} - \frac{1}{T_f}\right]$$

The above expression can very easily be rearranged to give finally

$$\Delta S_{tot}(T_f) = \Delta S_{tot}(T_i) + \Delta_r H^\circ \left[\frac{1}{T_i} - \frac{1}{T_f}\right] \qquad (6)$$

This is our extended van't Hoff equation, which may also be called the total entropy equation.

3. Discussion

The effect of temperature on equillibria of exothermic and endothermic processes can be very generally explained by the extended van't Hoff equation, equation (6). For example, for exothermic processes, processes that are accompanied by evolution of energy as heat, equation (6) predicts a decrease in total entropy change ΔS_{tot} as the temperature is increased. Hence the observed favoring of reactants over products as the temperature gets increased in an exothermic reaction. On the other hand for endothermic processes, processes that are accompanied by absorption of energy as heat, equation (6) predicts an increase in total entropy change ΔS_{tot} as the temperature gets increased. Hence the observed favoring of products over reactants as the temperature is increased in an endothermic process. This must be so because $\Delta_r H^\circ < 0$ for an exothermic system while $\Delta_r H^\circ > 0$ for an endothermic system. One can carry out a similar kind of analysis as the temperature is lowered for both endothermic as well as exothermic processes. One can also look at the predictions of equation (6) in another way by taking equation (5) also into consideration. Since as per equation (6) an increase of temperature leads to a decrease in total entropy change for an exothermic process, the equilibrium constant decreases with increase of temperature as per equation (5). Similarly, since for an endothermic process an increase of temperature, according to equation (6), leads to an increase in total entropy change, the equilibrium constant for an endothermic process increases with increase of temperature as per equation (5). In fact one can quantitatively determine, using equation (5), by how much the value of K_{eq} changes. One can also explain the observed drastic shift in the value of equilibrium constant as the temperature of a system is varied by a few hundred degrees (as is usually the case in real world processes like the Haber-Bosch process [12] used in the manufacture of ammonia) on the basis of the fact that the relationship involved between K_{eq} and ΔS_{tot} in equation (5) is an exponential one and therefore the observed behavior has something to do with the nature of the exponential function. This is one of the novel predictions of equation (5).

4. Conclusion

A more fundamental thermodynamic explanation of the behavior of equilibrium constant towards temperature for both exothermic and endothermic processes (reactions) relies on the relative importance of the magnitudes of the entropy changes of the reaction system and its surroundings; in other words on the total entropy change. Hence it is desirable to

have a quantitative expression underlying this explanation. It is possible to extend van't Hoff's equation to arrive at a mathematical expression that can serve and provide a quantitative theoretical basis to the stated explanation just like van't Hoff's original equation provides a theoretical basis to the explanation of dependence of equilibrium constant on temperature through the use of Gibbs energy change.

Conflict of Interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be considered as a potential conflict of interest.

Acknowledgements

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