

Van't Hoff's Law in terms of Entropy

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Abstract

We show that well-known van't Hoff's law in chemical thermodynamics can be expressed in terms of the total entropy change by making use of the Gibbs-Helmholtz equation and the relationship between Gibbs energy and total entropy. The resulting expression provides the theoretical underpinnings of the explanation of the effect of temperature on equilibria in terms of total entropy just as conventional Van't Hoff's law provides a theoretical basis for an explanation based on the idea of free energy. Both exothermic and endothermic cases are discussed and the central role that the total entropy change plays in determining the dependence of equilibrium constant K on temperature T has been emphasized.

Keywords: : Van't Hoff's law, Gibbs-Helmholtz equation, Gibbs energy, Equilibrium constant, Entropy

Introduction

The entropic formulation of Van't Hoff's law was discovered [1], by this author a few years ago and in the subsequent years its interpretation and significance was discussed in detail elsewhere [2,3]. The aim of present paper is to bring together both the mathematical and theoretical aspects of this law for the sake of convenience of understanding and application. We thus begin, in the next section, by first introducing the conventional Van't Hoff equation and show, in particular, how it is usually derived by making use of the Gibbs-Helmholtz equation and the Van't Hoff isotherm [4-7]. We then, in a subsequent section, derive an alternative formulation of the law in terms of entropy. We do this by taking a well-known, and very important, result from the Second law of thermodynamics concerning free energy and substituting it in the Gibbs-Helmholtz equation [1]. Finally, we present an interpretation of our new Van't Hoff equation and also discuss its significance.

The conventional Van't Hoff's law

A crucially important result in chemical thermodynamics is the Gibbs-Helmholtz equation [4], usually expressed, at a constant standard pressure of one bar, as

$$\frac{\partial(\Delta_r G^\circ/T)}{\partial T} = -\frac{\Delta_r H^\circ}{T^2} \quad (1)$$

The conventional expression for Van't Hoff's law can be derived from this equation if we take the Van't Hoff isotherm, $\Delta_r G^\circ = -RT \ln K$ and substitute it on its right hand side. This substitution then results in the following expression

$$d \ln K = \frac{\Delta_r H^\circ}{RT^2} dT \quad (2)$$

One can also integrate equation (2) between the initial and final states of the system to yield the following expression

$$\ln \frac{K(T_f)}{K(T_i)} = \int_{T_i}^{T_f} \frac{\Delta_r H^\circ}{RT^2} dT \quad (3)$$

From which the usual expression for Van't Hoff's law is easily obtained by treating the enthalpy as constant for the temperature range of interest [4].

$$\ln \frac{K(T_f)}{K(T_i)} = \frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_i} - \frac{1}{T_f} \right] \quad (4)$$

The Van't Hoff equation (4) is commonly employed to determine the variation of an equilibrium constant K with temperature [4-7]. This effect of temperature on the equilibrium constant is usually understood through its effect on the standard Gibbs energy of reaction $\Delta_r G^\circ$. In other words, any change in K with T is perceived as a change in the value of the standard Gibbs energy of reaction $\Delta_r G^\circ$ [4]. Furthermore, the dependence of K on temperature is determined by the sign of $\Delta_r H^\circ$ and the Van't Hoff equation provides the theoretical basis of this dependence. However, the effect of temperature on equilibria has also been discussed in terms of the importance of relative magnitudes of the entropy changes of the system and its immediate surroundings [4] by employing the following relation,

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \quad (5)$$

It is with this interpretation in mind that the Van't Hoff equation was formulated in terms of entropy [1,2] to yield an expression that highlights in a more direct manner the role that total entropy change plays in determining the direction of the reaction at equilibrium [1].

The entropy formulation of Van't Hoff's law

If we multiply both sides of equation (5) by $-\frac{1}{T}$ we obtain

$$-\frac{\Delta_r G^\circ}{T} = -\frac{\Delta_r H^\circ}{T} + \Delta_r S^\circ \quad (6)$$

We identify the first term on the right hand side of above equation with the entropy change of the surroundings [4] and denote it by $\Delta_r S_{sur}$, that is

$$\Delta_r S_{sur} = -\frac{\Delta_r H^\circ}{T}$$

and realize that since $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$, we obtain

$$\Delta_r G^\circ = -T\Delta_r S_{tot} \quad (7)$$

Here $\Delta_r S_{tot}$ is the total entropy change that the reaction generates and T denotes the absolute temperature. In order to fully appreciate the role of entropy in determining the direction of reaction process at equilibrium we now substitute Eq. (7) into the Gibbs-Helmholtz equation given in the beginning and obtain

$$\frac{\partial \Delta_r S_{tot}}{\partial T} = \frac{\Delta_r H^\circ}{T^2} \quad (8)$$

Equation (8) is the Van't Hoff's law in terms of entropy. It can be directly integrated between two specified initial and final states of the system to give

$$\Delta_r S_{tot}(T_f) = \Delta_r S_{tot}(T_i) + \int_{T_i}^{T_f} \frac{\Delta_r H^\circ}{T^2} dT \quad (9)$$

One can carry out the integration in above equation further provided one knows how the enthalpy of the system varies with temperature [4]. If one uses the approximation that the standard reaction enthalpy is independent of temperature, a valid approximation for at least small ranges of temperature [4], then Eq. (9) can be easily integrated to give

$$\Delta_r S_{tot}(T_f) = \Delta_r S_{tot}(T_i) + \Delta_r H^\circ \left[\frac{1}{T_i} - \frac{1}{T_f} \right] \quad (10)$$

Both equations (9) and (10) are formulations of Van't Hoff's law in terms of entropy and their significance is discussed in the next section.

Significance of the entropy formulation

As has been mentioned in the previous section, the effect of temperature on equilibria has also been discussed [4], in a more general manner, in terms of the importance of relative magnitudes of the entropy changes of the system and its surroundings by employing equation (5). Thus, when the reaction proceeds with the evolution of energy as heat the term $-\frac{\Delta_r H^\circ}{T}$ will contribute a positive entropy change to the surroundings. This will shift the equilibrium in the forward direction and favor the formation of products. When the temperature is lowered this contribution due to $-\frac{\Delta_r H^\circ}{T}$ also becomes fairly large. For a decrease in temperature the magnitude of $-\frac{\Delta_r H^\circ}{T}$ term also decreases. At higher temperatures the extent of decrease is such that the importance of the increasing entropy of the surroundings has a less significant role to play. Consequently, the equilibrium in such cases lies less towards the product side and the value of equilibrium constant decreases. For a reaction that proceeds with the absorption of energy as heat the main contributing factor is increase in entropy of the system due to the energy as heat soaked up from the surroundings. The importance of the unfavorable entropy change of the surroundings $\Delta_r S_{sur} = -\frac{\Delta_r H^\circ}{T}$ gets reduced when the temperature is increased and the reaction shifts towards the product side. Since entropy is a fundamental property of the universe, the increase in entropy is a more fundamental origin of the behavior equilibria towards temperature. It is therefore desirable to have a mathematical expression underlying this entropy based explanation of equilibria. As has been explicitly demonstrated above, it is possible to derive an alternative formula for the Van't Hoff equation in terms of entropy which provides a theoretical basis for the entropy-based explanation just as the conventional formulation provides the theoretical underpinnings of the explanation based on the concept of free energy.

Discussion

A very useful expression in chemistry to quantitatively determine the variation of equilibrium constant K with temperature is the Van't Hoff's law or the so-called Van't Hoff equation usually represented by Eq. (4). In essence Eq. (4) 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. The physical basis behind the variation of equilibrium constant with temperature is usually discussed in terms of the effect of T on the standard reaction Gibbs energy $\Delta_r G^\circ$. The actual dependence of K on temperature depends on the sign of $\Delta_r H^\circ$ and the van't Hoff equation provides a theoretical basis of this dependence. However, another more general way to look at the effect is in terms of the total entropy change $\Delta_r S_{tot}$ that the reaction system causes [4]. In other words, one takes into consideration the importance of the relative entropy changes of the reaction system and its immediate surroundings. It thus becomes desirable to have a theoretical expression underlying this total entropy-based explanation. It turns out that it is possible to derive a form of Van't Hoff equation in terms of total entropy and which one may call the total entropy equation. To this end one can use the Gibbs-Helmholtz equation and the definition of Gibbs energy to arrive at a result expressed by Eq. (10). The effect of temperature on equilibria of exothermic and endothermic is then explained in a more fundamental and general way by this new Van't Hoff type equation. For reactions that are accompanied by evolution of energy as heat (exothermic reactions), Eq. (10) predicts a decrease in total entropy $\Delta_r S_{tot}$ as one increases the temperature. Hence the favorable condition for an exothermic reaction will be a decrease in temperature. For reactions that are accompanied by absorption of energy as heat (endothermic reactions), Eq. (10) predicts an increase in total entropy $\Delta_r S_{tot}$ as the temperature is increased. Hence the favorable condition for an endothermic reaction will be an increase of temperature.

Conclusion

An explanation of the behavior of equilibria towards temperature for both exothermic and endothermic reactions relies on the importance of the relative entropy changes of the reaction system and its surroundings; in other words, on the total entropy change. It thus becomes desirable to have a theoretical expression underlying this explanation. It is possible to derive an expression for Van't Hoff's law, in terms of total entropy change, that can provide a theoretical basis for the stated explanation just as conventional Van't Hoff's law provides a theoretical basis for an explanation based on the concept of free energy.

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.

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