Answer on Question #75449 - Chemistry - Physical Chemistry

Question:

Derive the expression relating equilibrium constant with temperature.

Solution:

Since the rate constant of the chemical reaction depends only on the temperature, it is evident that the equilibrium constant depends only on the temperature. Substituting in the expression for the equilibrium constant the values of the rate constants of the forward and backward reactions from the Arrhenius equation and performing simple transformations, one can obtain

$Kp = k_1 / k_2 = (A_1 / A_2) e^{-(E_2-E_1) / RT} = Ae^{-DE / RT}$

where A_1 and A_2, E_1 and E_2 are respectively the pre-exponential factors and activation energies of the direct and reverse reactions, and DE is the difference between the activation energies of the reverse and direct reactions. This difference corresponds to the thermal effect of the reaction. Then the dependence of the equilibrium constant on temperature will be expressed by the equation:

$Kp = Ae^{Q / RT}$

Let us show the possibilities of using the Van't Hoff equation for determining the equilibrium constant at different temperatures and calculating the thermal effect of the reaction.

We logarithm the equation

$lgKp = Q / (2,303 RT) + lgA$ or $lgKp = (Q / (2.303 R)) (1 / T) + lgA$

The last expression represents the equation of a straight line in coordinates lgKp - 1 / T:

If we plot the plot of lgKp versus 1 / T, then the obtained experimental straight line cuts off on the ordinate axis a segment equal to lgA and having a slope equal to Q / (2,303RT), whence it is possible to determine Q.

If we assume that the thermal effect of the reaction does not depend on temperature, which is permissible in small temperature ranges, then knowing the equilibrium constant at one temperature (T_1), we can determine the equilibrium constant at any other temperature (T_2).

Let us write the expressions for the equilibrium constant for temperatures T_1 and T_2:

$lgKp_1 = Q / (2,303RT_1) + lgA$, $lgKp_2 = Q / (2,303RT_2) + lgA$.

Subtracting the second equation from the first, we get:

$lg (Kp_1/Kp_2) = (Q / (2,303R)) (1/T_1-1/T_2)$.