Temperature Effects on Equilibrium: A Study Guide

Discussion Questions

- How does temperature affect Gibb's energy?
- How does temperature affect and equilibrium?

Temperature Effects on Equilibrium

For convenience, we treat temperature, entropy, enthalpy, and Gibb's energy as general state functions and represent them by $T$, $S$, $H$, and $G$ respectively, dropping the change symbol $D$, associated with them. The justification for doing these have been introduced in Gibb's energy.

Since $S$, $H$, and $G$ depends on $T$, temperature affects chemical reactions and chemical equilibria. We discuss the temperature effects in general terms, and the strategy introduced here may be useful for solving complicated problems later.

How does temperature affect Gibb's energy?

Gibb's energy, $G$, is a general state function defined in terms of state functions entropy $S$ and enthalpy $H$. It's relationship with the equilibrium constant $K$ has also been defined using the formula below. This notations are widely used in the field of thermodynamics.

$$
G = H - T S
= - R T \ln K
$$

For entropy, we have defined the standard or absolute entropy $S^0$ as

$$S^0 = S^0_{298} C_p \frac{dT}{T}
$$

The symbol $C_p$ is the heat capacity at constant pressure, it also depends on $T$, not a constant.

Thermodynamic data usually lists standard enthalpy $H^0$, and standard entropy $S^0$. When measured at temperature $T$ other than 298 K, their values are given by

$$DS = S^0 + C_p \frac{T_{298}}{T} dt / T
= S^0 + C_p \ln (298/T)
$$

$$DH = H^0 + C_p T_{298} \frac{dT}{T}
= H^0 + C_p (T - 298)
$$

The integrations given above are valid only if $C_p$ is a constant between 298 and $T$ K. If the temperature range is large, an
integration process either by mathematical means or by numerical means should be carried out. Within small ranges, the assumption is reasonable, especially if average values are used. Under the circumstance,

$$DG = G^0 + C_p \ln \left( \frac{298}{T} \right) + C_p (T - 298)$$

$$= - R T \ln K$$

The above model shows that Gibb's energy depends on temperature. This formulation is true if $C_p$ is a constant between 298 and $T$ K. In general, the heat capacity varies with temperature and the variation should not be ignored if the temperature range is very large. In some cases, an average value for the heat capacity may be used.

Gibb's free energies of a system drive both physical and chemical changes. For physical changes, the heat capacities of the system over the ranges of temperature should be considered. In cases of chemical reactions, the differences in heat capacity between products and reactants shall be considered.

How does temperature affect equilibrium?

For chemical reactions, the differences in heat capacity between the products and the reactants $D C_p$ are to be used. Using the equation derived previously,

$$DG = G^0 + D C_p \ln \left( \frac{298}{T} \right) + D C_p (T - 298)$$

$$= - R T \ln K,$$

the effect of temperature on the equilibrium constant $K$ can be derived,

$$\ln K = - \frac{DG^0}{R T} - \frac{C_p}{(R T)} \left[ 298 - T + \ln \left( \frac{298}{T} \right) \right]$$

Recall that $K^0$ is the equilibrium constant at 298 K. The equation can be simplified to give,

$$\ln \left( \frac{K}{K^0} \right) = - \frac{C_p}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \left[ T_1 - T_2 + \ln \left( \frac{T_1}{T_2} \right) \right]$$

And to generalize it, if $K_1$ and $K_2$ are equilibrium constants at $T_1$ and $T_2$ respectively, we can derive the formula,

$$\ln \left( \frac{K_2}{K_1} \right) = - \frac{C_p}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \left[ T_1 - T_2 + \ln \left( \frac{T_1}{T_2} \right) \right]$$

By measuring the equilibrium constants at different temperatures and using this equation, we may estimate the heat capacities over ranges of temperatures. Note that

$$C_p(T_1 - T_2) = DH$$

And if we ignore the term $\ln \left( \frac{T_1}{T_2} \right)$, the above equation is the same as the familiar Helmholtz equation, which is discussed in Example 1 below.

Example 1
The Gibbs-Helmholtz equation is
\[ \frac{d(G / T)}{dT} = - \frac{DH}{T^2}. \]

Show that
\[ \frac{DH}{d \ln K} = - \frac{1}{R} \frac{d}{dT}(1/T) \]

**SOLUTION**
Since
\[ DG = - RT \ln K, \]
\[ \ln K = - \frac{DG}{RT} \]

Differentiate both sides with respect to \((1/T)\) in the above equation gives,
\[ \frac{d(\ln K)}{dT} = \frac{-1}{R} \frac{d(DG / T)}{dT} \]
\[ = - \frac{DH}{R T^2} \]

**DISCUSSION**
If \(K_1\) and \(K_2\) are the equilibrium constant at \(T_1\) and \(T_2\) respectively, show further that
\[ \ln \left( \frac{K_1}{K_2} \right) = - \left( \frac{DH}{R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \]

This is achieved by definite integral. This relationship indicates that the plot of \(\ln K\) versus \(1/T\) is a straight line, and the slope is \(-\left(\frac{DH}{R}\right)\). Thus, \(DH\) can be determined by measuring the equilibrium constant at different temperatures.

**Example 2**
The vapour pressure of water at 298 K is 23.756 mmHg. Estimate the molar standard Gibb's energy.

**SOLUTION**
The vapour pressure of 23.756 mmHg should be converted to a pressure in units of pascal \((N m^{-2})\),
\[ \frac{101,300 \text{ N m}^{-2}}{23.756 \text{ mmHg}} \approx 3166 \text{ Pa} \]
\[ 760 \text{ mmHg} \]

\[ G^0 = 8.312 J \cdot 298 \ln(3166) \]
\[ = 20.0 \text{ kJ / hr} \]

**DISCUSSION**
This example illustrates the evaluation of Gibb's energy when the equilibrium constant is known.
Questions

1. **For a system that is at equilibrium, what is the Gibb's free energy of the system?**

   **Skill** -
   Explain the physical meaning of Gibb's free energy in terms of changes.

2. **The standard enthalpies of H₂O (g) and H₂O (l) given in a Table of Chemical Thermodynamic Data are -242 and -286 kJ mol⁻¹ respectively. What is the heat of vaporization?**

   **Skill** - Construct cycles by applying Hess's law to evaluate the energy changes for a chemical or physical process, such as

   \[
   \begin{align*}
   H_2(g) + \frac{1}{2}O_2(g) &\quad | -242 \quad | \\
   &\quad | -286 \quad | \\
   H_2O(g) &\quad | \\
   &\quad | H=? \quad | \\
   &\quad | \quad | \\
   \sim H_2O(l) &\quad | 
   \end{align*}
   \]

   Note that the heat of vaporization so calculated is the heat of vaporization at 298 K.

Solutions

1. At equilibrium, there is no net change, and G = 0.

Contributors

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