Gibbs–Helmholtz equation

The **Gibbs–Helmholtz equation** is a thermodynamic equation used for calculating changes in the Gibbs energy of a system as a function of temperature. It is named after Josiah Willard Gibbs and Hermann von Helmholtz.

Equation

The equation is

$$\boxed{\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2},}$$

where *H* is the enthalpy, *T* the absolute temperature and *G* the Gibbs free energy of the system, all at constant pressure *p*. The equation states that the change in the *G/T* ratio at constant pressure as a result of an infinitesimally small change in temperature is a factor H/T^2..

Chemical reactions

The typical applications are to chemical reactions. The equation reads:[2]

$$\left(\frac{\partial (\Delta G^\ominus/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

with Δ*G* as the change in Gibbs energy and Δ*H* as the enthalpy change (considered independent of temperature). The ⦵ denotes standard pressure (1 bar).

Integrating with respect to *T* (again *p* is constant) it becomes:

$$\frac{\Delta G^\ominus(T_2)}{T_2} - \frac{\Delta G^\ominus(T_1)}{T_1} = \Delta H^\ominus(p)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation quickly enables the calculation of the Gibbs free energy change for a chemical reaction at any temperature T_2 with knowledge of just the Standard Gibbs free energy change of formation and the Standard enthalpy change of formation for the individual components.

Also, using the reaction isotherm equation, that is

$$\frac{\Delta G^\ominus}{T} = -R \ln K$$

which relates the Gibbs energy to a chemical equilibrium constant, the van 't Hoff equation can be derived.

Derivation

Background

The definition of the Gibbs function is

$$H = G + ST$$

where *H* is the enthalpy defined by:

$$H = U + pV$$

Taking differentials of each definition to find *dH* and *dG*, then using the fundamental thermodynamic relation (always true for reversible or irreversible processes):

$$dU = T\,dS - p\,dV$$

where *S* is the entropy, *V* is volume, (minus sign due to reversibility, in which *dU* = 0: work other than pressure-volume may be done and is equal to −*pV*) leads to the "reversed" form of the initial fundamental relation into a new master equation:

$$dG = -S\,dT + V\,dp$$

This is the Gibbs free energy for a closed system. The Gibbs–Helmholtz equation can be derived by this second master equation, and the chain rule for partial derivative

Gibbs free energy and Temperature: The Gibbs-Helmholtz Equation

Frequently we wish to run reactions at temperatures other than 25^{o}C. Since we know that the change in the Gibbs free energy, $\Delta_r G^{o}$, between products and reactants tells us whether or not the reaction will run spontaneously we will need this quantity at the new temperature.

(Reminder: If $\Delta_r G^{o} < 0$ the reaction is spontaneous and if $\Delta_r G^{o} > 0$ the reaction is not spontaneous.)

We also know that there are two components to $\Delta_r G^{o}$. That is, $\Delta_r G^{o} = \Delta_r H^{o} - T\Delta_r S^{o}$, where the $\Delta_r H^{o}$ term is only weakly dependent on temperature, but the $T\Delta_r S^{o}$ term is strongly dependent on temperature due to the presence of the T in the term.

So the question becomes, how do these things balance out? What is the dependence of $\Delta_r G^{o}$ on temperature? The simple answer is obtained from the derivative of G with respect to T.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S. \qquad (1)$$

If we apply Equation 1 to $\Delta_r G^{o} = G^{o}_{\text{products}} - G^{o}_{\text{reactants}}$ we get,

$$\begin{aligned}\left(\frac{\partial \Delta_r G^{o}}{\partial T}\right)_p &= \left(\frac{\partial G^{o}_{\text{products}}}{\partial T}\right)_p - \left(\frac{\partial G^{o}_{\text{reactants}}}{\partial T}\right)_p \\ &= -S^{o}_{\text{products}} - \left(-S^{o}_{\text{reactants}}\right) \\ &= -\Delta_r S^{o}. \end{aligned} \qquad \text{(2a, b, c)}$$

Equation 2c shows that if $\Delta_r S^{o}$ is positive $\Delta_r G^{o}$ decreases with temperature, but if $\Delta_r S^{o}$ is negative $\Delta_r G^{o}$ increases with temperature. This will tell us whether $\Delta_r G^{o}$ increases or decreases with increasing temperature.

However, if we want to know whether or not a reaction is favored by an increase or decrease in temperature we really need to be looking at the equilibrium constant. If the equilibrium constant increases with temperature the reaction becomes more favored, but if the equilibrium constant decreases with temperature the reaction becomes less favored.

We will show later that the equilibrium constant for a chemical reaction depends on $\Delta_r G^{o}/T$ and not on $\Delta_r G^{o}$ all by itself. (There is a good reason for this which we will discuss below.) The Gibbs-Helmholtz equation addresses the question as to how $\Delta_r G^{o}/T$ changes with temperature. The Gibbs-Helmholtz equation can be presented in two different, but equivalent forms. If we are just worrying about *G* itself the two forms look like,

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = H, \qquad (3a)$$

and

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p = -\frac{H}{T^2}. \qquad (3b)$$

Or, applying the procedure we used in Equations 2a, b, and c, we can write,

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = \Delta H, \qquad (3c)$$

and

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}. \qquad (3d)$$

We won't derive any of these equations because the derivation is not particularly instructive. We will just show that the version of Equation 3a is true. (On the way you will also see why Equation 3b is true.)

Start with the left-hand side of Equation 3a and show that it is equivalent to the definition of Gibbs free energy:

$$
\begin{aligned}
\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p &= \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p \left(\frac{dT}{d\left(\frac{1}{T}\right)}\right) \\
&= \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p \frac{1}{\frac{d\left(\frac{1}{T}\right)}{dT}} \\
&= \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p \frac{1}{-\frac{1}{T^2}} \\
&= -T^2\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p \\
&= -T^2\left(+\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{1}{T^2}G\right) \\
&= -T\left(\frac{\partial G}{\partial T}\right)_p + G \\
&= -T(-S) + G \\
&= G + TS \\
&= H.
\end{aligned}
$$

We could easily substitute ΔG for G and end up with ΔH in the above sequence of equations.

So what is this good for? We will see that it is tremendously useful after we know the relationship between the equilibrium constant and $\Delta_r G^{o}/T$, but for now let's use the Gibbs-Helmholtz equation to calculate $\Delta_r G^{o}$ at a temperature, T_2 other than 25°C (which we will call T_1.

Set up Equation 3c for integration.

$$\left(\frac{\partial\left(\frac{\Delta_r G^\circ}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = \Delta_r H^\circ, \qquad (4)$$

$$d\left(\frac{\Delta_r G^\circ}{T}\right) = \Delta_r H^\circ d\left(\frac{1}{T}\right). \qquad (5)$$

Equation 5 integrates to give,

$$\left(\frac{\Delta_r G^\circ}{T}\right)_{T_2} - \left(\frac{\Delta_r G^\circ}{T}\right)_{T_1} = \int_{T_1}^{T_2} \Delta_r H^\circ d\left(\frac{1}{T}\right). \qquad (6)$$

To carry out the integration on the right-hand side of Equation 6 we would need to know how the heat of reaction changes with temperature. This information can be obtained if we know the heat capacities of the reactants and products as functions of temperature. However, usually the heat of reaction varies slowly with temperature so that it is a good approximation to regard the heat of reaction as constant.

Notice that Equation 5 is trivial to integrate if we make the approximation that $\Delta_r H^\circ$ is constant. With this approximation, Equation 5 integrates to,

$$\left(\frac{\Delta_r G^\circ}{T}\right)_{T_2} - \left(\frac{\Delta_r G^\circ}{T}\right)_{T_1} = \Delta_r H^\circ \int_{T_1}^{T_2} d\left(\frac{1}{T}\right), \qquad (7)$$

or,

$$\left(\frac{\Delta_r G^\circ}{T}\right)_{T_2} = \left(\frac{\Delta_r G^\circ}{T}\right)_{T_1} + \Delta_r H^\circ \left(\frac{1}{T_2} - \frac{1}{T_1}\right). \qquad (8)$$

We will apply Equation 8 to calculate ΔG for the freezing of super-cooled water at -20°C. The process is,

$H_2O(l, -20^\circ C) \rightarrow H_2O(s, -20^\circ C)$.

Do we know ΔG for this process at 0°C? Note that freezing water at its normal melting point is a reversible process so that the heat of fusion is a reversible heat at constant temperature. Therefore,

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}. \qquad (9)$$

Then

$$\begin{aligned} \Delta G_{\text{fus}} &= \Delta H_{\text{fus}} - T_{\text{fus}} \Delta S_{\text{fus}} \\ &= \Delta H_{\text{fus}} - T_{\text{fus}} \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} \\ &= 0. \end{aligned} \qquad (10a, b, c)$$

Equation 8, for our problem, becomes,

$$\begin{aligned} \left(\frac{\Delta G}{T}\right)_{T_2} &= \left(\frac{\Delta G}{T}\right)_{T_1} + \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &= 0 - \Delta H_{\text{fus}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \end{aligned}$$

$$\left(\frac{\Delta G}{253.15\text{ K}}\right) = -6008\text{ J}\left(\frac{1}{253.15\text{ K}} - \frac{1}{273.15\text{ K}}\right).$$

Then ΔG is − 440 J which is what we would expect because freezing super-cooled water is a spontaneous (and irreversible) process at − 20°C.

Why $\Delta G/T$?

We said above that $\Delta_r G^o$ tells us whether or not a reaction wants to go, but that the equilibrium constant, the ultimate arbiter of how strongly the reaction wants to go, depends on $\Delta_r G^o/T$. We will prove this statement later, but for now it might be interesting to see why that might be. Consider any process at constant temperature and pressure. We know that if T and p are constant then,

$$\Delta G = \Delta H - T\Delta S. \qquad (11)$$

Let's divide Equation 11 by T to see what $\Delta G/T$ looks like,

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S. \qquad (12)$$

Note that ΔH and ΔS in Equation 12 refer to things happening in the system. Rewrite Equation 12 to indicate that this is true,

$$\frac{\Delta G}{T} = \frac{\Delta H_{sys}}{T} - \Delta S_{sys}. \qquad (13)$$

Now, ΔH_{sys} is heat absorbed by the system. Where did this heat come from? It had to come from the surroundings so.

$$\begin{aligned} \Delta H_{surr} &= -\Delta H_{sys} \\ \Delta H_{sys} &= -\Delta H_{surr}. \end{aligned} \qquad (14a, b)$$

Most likely our process is irreversibly, but that doesn't matter because H is a state function so that ΔH is independent of path. We can always find a reversibly path to change the enthalpy of the surroundings by an amount ΔH_{surr}. (Our process is at constant temperature and pressure so that ΔH in both cases is a heat at constant pressure.) If we add heat ΔH_{surr} to the surroundings isothermally and reversibly then the entropy change in the surroundings is

$$\begin{aligned} \Delta S_{surr} &= \frac{\Delta H_{surr}}{T} \\ &= -\frac{\Delta H_{sys}}{T}, \end{aligned} \qquad (15a, b)$$

or

$$\frac{\Delta H_{sys}}{T} = -\Delta S_{surr}. \qquad (16)$$

Applying the result of Equation 16 to Equation 13 we find that,

$$\begin{aligned} \frac{\Delta G}{T} &= -\Delta S_{surr} - \Delta S_{sys} \\ &= -\Delta S_{universe}. \end{aligned} \qquad (17a, b)$$

Equation 17b tells us several things. It tells us that, in the final analysis, the ultimate driving force in nature is entropy, that is, the drive toward disorder. The system plus the surroundings is a closed isolated system so that the only spontaneous processes allowed are those which increase the entropy. Secondly, it explains why $\Delta G/T$ is more important than simply ΔG in determining how strongly spontaneous a process is. It is $-\Delta G/T$ which is related to the entropy change of the universe, not ΔG directly. Equation 17b also shows that the Gibbs free energy manages to include the entropy effects in the surroundings without ever telling us that it is doing so.