The Second Law: the machinery

The Gibbs energy, G, is of central importance in chemistry. At constant temperature and pressure, a system tends to adjust such as to minimize the value of G. Therefore, the equilibrium state of a system corresponds to the state of minimum Gibbs energy. Hence, to know how the equilibrium state responds to changes in conditions (for example, how a melting temperature responds to changes in pressure or the equilibrium composition of a reaction mixture responds to changes in temperature), we need to know how G varies.

Combining the First and Second Laws The fundamental equation

The First Law: dU = dq + dwFor a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work, $dw_{rev} = -pdV$ $dq_{rev} = TdS$

Therefore, for a reversible change in a closed system

dU = TdS - pdV fundamental equation

Because dU is an exact differential, its value in independent of path and the same value of dU is obtained whether the change is brought about irreversibly or reversibly. Consequently, *the equation applies to any change* – *reversible or irreversible* – *of a closed system that does no additional (non-expansion) work*. This combination of the First and Second Laws is called the **fundamental equation**.

Each term of the equation remains equal to the heat and work, respectively, only for a reversible change. If a process is irreversible, TdS > dq (the Clausius inequality) and -pdV < dw. However, the sum of dq and dw remains the same, provided the composition is constant.

Properties of the internal energy

The internal energy of a closed system changes in a simple way when either S or V is changed ($dU \propto dS$ and $dU \propto dV$). Thus, U should be regarded as a function of S and V. We could regard U as a function of other variables, such as S and p or T and V, because they are all interrelated; but the simplicity of the fundamental equation suggests that U(S,V) is the best choice.

The differential of U then can be written as

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V} dS + \left(\frac{\partial U}{\partial V}\right)_{S} dV$$
$$\left(\frac{\partial U}{\partial S}\right)_{V} = T \qquad \qquad \left(\frac{\partial U}{\partial V}\right)_{S} = -p$$

The first equation – a purely thermodynamic definition of temperature as the ratio of the changes in the internal energy and entropy of a constant-volume, closed, constant composition system.

The Maxwell relations

Suppose we can write an infinitesimal change in a function f(x,y) as df = gdx + hdywhere g and h are also functions of x and y. Then, the mathematical criterion of df to be an exact

differential is

$$\left(\frac{\partial g}{\partial y}\right)_{x} = \left(\frac{\partial h}{\partial x}\right)_{y}$$

The fundamental equation is an expression for an exact differential. Therefore, have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$
 a Maxwell relation

We can use the fact that H, G, and A are all state functions to derive three more Maxwell relations.

$$dU = TdS - pdV \qquad \left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial p}{\partial S}\right)_{V}$$
$$dH = TdS + Vdp \qquad \left(\frac{\partial T}{\partial p}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{p}$$
$$dA = -pdV - SdT \qquad \left(\frac{\partial p}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T}$$
$$dG = Vdp - SdT \qquad \left(\frac{\partial V}{\partial T}\right)_{p} = -\left(\frac{\partial S}{\partial p}\right)_{T}$$

The variation of internal energy with volume

The coefficient π_T (internal pressure), $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$, shows how the internal energy changes

as the volume of a system is changed isothermally. We can show now that

$$\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

thermodynamic equation of state

An expression for pressure in terms of a variety of thermodynamic properties of the system. We can derive it now by using a Maxwell relation.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V} dS + \left(\frac{\partial U}{\partial V}\right)_{S} dV \quad \text{divide both sides by } dV \text{ at const. } T:$$
$$\left(\frac{\partial U}{\partial V}\right)_{T} = \left(\frac{\partial U}{\partial S}\right)_{V} \left(\frac{\partial S}{\partial V}\right)_{T} + \left(\frac{\partial U}{\partial V}\right)_{S} \qquad \left(\frac{\partial U}{\partial S}\right)_{V} = T \qquad \left(\frac{\partial U}{\partial V}\right)_{S} = -p$$
$$\pi_{T} = \left(\frac{\partial U}{\partial V}\right)_{T} = T \left(\frac{\partial p}{\partial T}\right)_{V} - p$$

Example 1. Deriving a thermodynamical relation.

Show thermodynamically that $\pi_T = 0$ for a perfect gas and compute its value for a van der Waals gas.

For a perfect gas, p = nRT/V $(\partial p/\partial T)_V = nR/V$ $\pi_T = nRT/V - p = 0$

The equation of state of a van der Waals gas is

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \qquad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nB}$$
$$\pi_T = \frac{nRT}{V - nB} - \frac{nRT}{V - nB} + a\frac{n^2}{V^2} = a\frac{n^2}{V^2}$$

This result implies that the internal energy of a van der Waals gas increases when it expands isothermally $((\partial U/\partial V)_T > 0)$, and the increase is related to the parameter *a*, which models the attractive interactions between the particles. A larger molecular volume corresponds to a greater separation between molecules and thus to weaker mean intermolecular attractions, so the total energy is greater.

Properties of the Gibbs energy General considerations

$$G = H - TS \qquad dG = dH - TdS - SdT$$

$$H = U + pV \qquad dH = dU + pdV + Vdp \qquad dU = TdS - pdV$$

$$dG = (TdS - pdV) + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT$$

G may be best regarded as a function of *p* and *T*: important in chemistry because *p* and *T* are usually the variables under our control. (∂G) (∂G)

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$





Because *S* is positive, *G* decreases when the temperature is raised at constant pressure and composition. *G* decreases most sharply when *S* is large.

The Gibbs energy of the gaseous phase of a substance, which has a high molar entropy, is more sensitive to *T* that its liquid and solid phases. Because *V* is positive, *G* always increases when the pressure of the system is increased at constant *T* and composition. V_m of gases are large and *G* is more sensitive to pressure for the gas phase of a substance than for its liquid and solid phases. *Example 2. Calculating the effect of pressure on the Gibbs energy.*

Calculate the change in the molar Gibss energy of (a) liquid water treated as an incompressible fluid and (b) water vapor treated as a perfect gas, when the pressure is increased isothermally from 1.0 bar to 2.0 bar at 298 K.

We obtain the change in molar Gibbs energy by integrating the equation for d*G* at constant temperature (dT = 0):

$$G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} V_m dp$$

(a) for the incompressible liquid, $V_{\rm m}$ is constant, 180.0 cm³ mol⁻¹:

$$G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} V_m dp = V_m(p_f - p_i) = +1.8 \text{ J mol}^{-1}$$

(b) For a perfect gas, $G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} \frac{RT}{p} dp = RT \ln \frac{p_f}{p_i} = +1.7 \text{ kJ mol}^{-1}$. *G* increases in

both cases, but for the gas the increase is ~ 1000 times greater.

The variation of the Gibbs energy with temperature

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

G/T is related to the total entropy change in a process and the variation of this quantity with temperature appears to be simpler than the temperature variation of G alone:

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

Gibbs-Helmholtz equation

If we know the enthalpy of the system, then we know how G/T varies with temperature.

$$\begin{pmatrix} \frac{\partial G}{\partial T} \end{pmatrix}_p - \frac{G}{T} = -\frac{H}{T} \qquad \qquad \left(\frac{\partial}{\partial T} \frac{G}{T} \right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p + G \frac{d}{dT} \frac{1}{T} = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2} = \frac{1}{T} \left\{ \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T} \right\} \\ \left(\frac{\partial}{\partial T} \frac{G}{T} \right)_p = \frac{1}{T} \left(-\frac{H}{T} \right) = -\frac{H}{T^2}$$

We can also use the chain rule: for a function f = f(g), where g = g(t), $\frac{df}{dt}$

$$\frac{df}{dt} = \frac{df}{dg}\frac{dg}{dt}$$

df da

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{p} = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_{p} \frac{d(1/T)}{dT} = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_{p} \times \left(-\frac{1}{T^{2}}\right) - \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_{p} \times \left(-\frac{1}{T^{2}}\right) = -\frac{H}{T^{2}} - \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_{p} = H$$

An alternative form of the Gibbs-Helmholtz equation

The Gibbs-Helmholtz equation is most useful when applied to changes. Because $\Delta G = G_f - G_i$,

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

The variation of Gibbs energy with pressure

To find the Gibbs energy at one pressure from its value at another pressure at constant *T*, we set dT = 0 and integrate:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$



Liquids and solids

For a liquid or solid, the volume changes only slightly with pressure and we can treat V as a constant. For molar quantities:

 $G_{\rm m}(p_{\rm f}) = G_{\rm m}(p_{\rm i}) + V_{\rm m}(p_{\rm f} - p_{\rm i}) = G_{\rm m}(p_{\rm i}) + V_{\rm m}\Delta p$

Under normal laboratory conditions $V_{\rm m}\Delta p$ is very small and may be neglected. Therefore, we usually may suppose that the Gibbs energies of solids and liquids are independent of pressure. Geophysical processes: pressures in the Earth's interior are huge – their effect on the Gibbs energies cannot be ignored.

Gases

The molar volumes of gases are large and the Gibbs energy of gas depends strongly on the pressure:

$$G(p_f) = G(p_i) + nRT \int_{p_i}^{p_f} \frac{dp}{p} = G(p_i) + nRT \ln \frac{p_f}{p_i}$$

When the pressure is increased tenfold at room temperature, the molar Gibbs energy increases by ~6 kJ mol⁻¹. If we set $p_i = p^{\emptyset}$ (the standard pressure of 1 bar, then the Gibbs energy of a perfect gas at a pressure *p* is related to its standard value as $G = G^{\emptyset} + nRT \ln(p/p^{\emptyset})$



Now we consider the pressure dependence of a real gas. We replace the true pressure *p* by an effective pressure called the **fugacity**, *f*: $G_{\rm m} = G_{\rm m}^{\varnothing} + RT \ln(f/p^{\varnothing})$

The fugacity is a function of the pressure and temperature and is defined so that this equation is exactly true. Later, we will derive thermodynamically exact expressions in terms of the Gibbs energy and in terms of fugacities.

The expressions in terms of fugacities are exact but they are useful only if we know how to relate fugacities to actual pressures:

$$f = \phi p$$

 ϕ - the **fugacity** coefficient (dimensionless) – related to the compression factor, Z, of the gas between p = 0 and the pressure of interest:

$$\ln\phi = \int_0^p \frac{Z-1}{p} dp$$

Derivation:

$$\int_{p'}^{p} V_m dp = G_m - G_{m'} = RT \ln \frac{f}{f'}$$

Perfect gas

$$\int_{p'}^{p} V_{perfect,m} dp = RT \ln \frac{p}{p'}$$
$$\int_{p'}^{p} \left(V_m - V_{perfect,m} \right) dp = RT \left(\ln \frac{f}{f'} - \ln \frac{p}{p'} \right)$$
$$\ln \left(\frac{f}{p} \times \frac{p'}{f'} \right) = \frac{1}{RT} \int_{p'}^{p} \left(V_m - V_{perfect,m} \right) dp$$

When $p' \rightarrow 0$, the gas behaves perfectly and f' = p': $f'/p' \rightarrow 1$ as $p' \rightarrow 0$. We take the limit f'/p' = 1 on the left and p' = 0 on the right:

$$\ln\frac{f}{p} = \frac{1}{RT} \int_{0}^{p} \left(V_{m} - V_{perfect,m}\right) dp \qquad \ln\phi = \frac{1}{RT} \int_{0}^{p} \left(V_{m} - V_{perfect,m}\right) dp$$
$$V_{m} = \frac{RTZ}{p} \qquad V_{perfect,m} = \frac{RT}{p} \qquad \ln\phi = \int_{0}^{p} \frac{Z - 1}{p} dp$$



For most gases, Z < 1 up to moderate pressures but Z > 1 at higher pressures. If Z < 1 throughout the range of integration, the integrand is negative and $\phi < 1 \Rightarrow f < p$ – the molecules tend to stick together and the molar Gibbs energy of the gas is less than that of a perfect gas. At higher pressures, the range over which Z > 1 may dominate the range over which Z < 1. The integral is then positive: $\phi > 1 \Rightarrow f > p$ – the repulsive interactions are dominant and tend to drive the particles apart – the molar Gibbs energy of the gas is greater than that of a perfect gas.



The figures (calculated using the van der Waals equation of state) show how the fugacity coefficient depends on the pressure in terms of the reduced variables. The curves are labeled with the reduced temperature $T_r = T/T_c$.