The Second Law: The Machinery

Chapter 5 of Atkins: The Second Law: The Concepts

Sections 5.1 - 5.6

Combining First and Second Laws
Properties of the Internal Energy
The Chemical Potential of a Pure Substance

Real Gases: The Fugacity
Definition of Fugacity
Standard States of Gases
Relation Between Fugacity and Pressure

Properties of Internal Energy

Reversible change: \( T \, dS = dq \) or \( -p \, dV \) same as \( dw \)
Irreversible change: \( T \, dS > dq \) (Clausius inequality), and \( -p \, dV > dw \)

Sum of \( dw = dq = \) Sum of \( T \, dS + -p \, dV \), system of constant composition

When \( S \) and \( V \) are changed, \( dw = dq \) and \( dS = dV \), from the fundamental equation, suggesting that \( dU \) should be written as a function of \( S \) and \( V \)

\[
\frac{dU}{dS} = \frac{T}{dV} \quad \frac{dU}{dV} = -p
\]

Thermodynamic definition of temperature

\[
\left( \frac{dU}{dS} \right)_p = T \quad \left( \frac{dU}{dV} \right)_T = -p
\]

Maxwell Relations

The state functions are exact differentials, meaning that they must pass the test that indicate their independence of path taken:

\[
df = gdx + hdy \text{ is exact if } \frac{\partial g}{\partial y}(x) = \frac{\partial h}{\partial x}(y)
\]

We know that \( dU = T \, dS - p \, dV \) is exact, so it follows that:

\[
\left( \frac{dT}{dV} \right)_p = \frac{\partial P}{\partial V}(S)
\]

A relationship between quantities that would not seem to be related on first sight, has been generated. In fact, the four Maxwell relations can be derived from the four state functions \( U, H, G \) and \( A \):

\[
\begin{align*}
\left( \frac{\partial T}{\partial V} \right)_p &= \frac{\partial P}{\partial V}(S) \\
\left( \frac{\partial P}{\partial T} \right)_V &= \frac{\partial S}{\partial V}(p) \\
\left( \frac{\partial S}{\partial P} \right)_T &= \frac{\partial V}{\partial P}(T) \\
\left( \frac{\partial V}{\partial S} \right)_P &= \frac{\partial P}{\partial T}(V)
\end{align*}
\]
Variation of Internal Energy with Volume

In Chapter 3, we defined a coefficient called the internal pressure
\[ \pi = \left( \frac{\partial U}{\partial V} \right)_T \]
which can be written as a thermodynamic equation of state. In terms of \( p \) and \( T \), and can therefore be applied to any substance. We said that we would prove that:

\[ \pi = T \frac{\partial ^2 U}{\partial V \partial T} - p \]

We can obtain \( \pi T \) by dividing the equation for \( dU \) by \( dV \) and substituting in:

\[ (\text{use a Maxwell relation}) \]

\[ \pi T = \left( \frac{\partial U}{\partial V} \right)_T \]

\[ \pi \]

Properties of the Gibbs Energy

Same arguments that apply for internal energy, \( U \), are applied to \( G \). When a system has a change of state resulting in \( \Delta G \), this results from changes in \( H, S, \) and \( T \). Again, for infinitesimal changes:

\[ dG = dh + pdV + Vdp \]

Since \( H = U + pV \):

\[ dh = dU + pdV + Vdp \]

\[ dG = (T dS - p dV) + pdV + Vdp - TdS - SdT \]

thus,

\[ dG = Vdp - SdT \]

Change in \( G \) is proportional to changes in pressure and temperature

Because we control \( p \) and \( T \), \( G \) is a very important quantity in chemistry. \( G \) carries the combined consequences of the 1st and 2nd laws!

Gibbs Energy, Pressure & Temperature

From the relationship below, we can derive two new partial derivatives

\[ \left( \frac{\partial G}{\partial T} \right)_p = -S \]

\( G \) decreases when the \( T \) is increased at constant \( p \), because \( S \) is positive.

\( G \) decreases most sharply when \( S \) large. If \( G \) of gaseous phase is more sensitive to \( T \) (then liquids or solids).

\( G \) increases when \( p \) is increased at constant \( T \) (since \( S \) is positive).

Temperature Dependence of \( G \)

In many chemical and physical transformations, the equilibrium composition of a system depends on the Gibbs energy, so we must know the response of the Gibbs energy to temperature changes.

Since \( \left( \frac{\partial G}{\partial T} \right)_p = -S \), we write

\[ \left( \frac{\partial G}{\partial T} \right)_p = -S = \frac{G - H}{T} \]

and we can rearrange to

\[ \left( \frac{\partial G}{\partial T} \right)_p = \frac{G - H}{T} \]

And now rewrite the LHS using:

\[ \left( \frac{\partial G}{\partial T} \right)_p \]

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Temperature Dependence of $G$

This results in the **Gibbs-Helmholz equation** (which relates $G$ and $H$):

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

(We shall see that we want the GH equation in this form, since the equilibrium constants of reactions are related to $G/T$ rather than just $G$)

Pressure Dependence of $G$

### Incompressible Fluid

(a) incompressible liquid, $V_m = $ constant

(b) perfect gas, $V_m = \frac{RT}{p}$

#### Part I

- $\Delta G = +ve$, though the increase for gas is 1000 times that for liquid

\[
\Delta G_\text{pf}(p_f) - \Delta G_\text{pi}(p_i) = \int_{p_i}^{p_f} V_m dp \\
= (8.0 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) \times (6.0 \times 10^5 \text{ Pa}) = 1.8 \text{ J mol}^{-1}
\]

\[
\Delta G_\text{pf}(p_f) - \Delta G_\text{pi}(p_i) = \int_{p_i}^{p_f} \frac{RT}{p} dp = RT \ln \left( \frac{p_f}{p_i} \right) \\
= (2.48 \text{ kJ mol}^{-1}) \times \ln(2.0) = 1.7 \text{ kJ mol}^{-1}
\]

### Solid & Liquid

For liquids and solids, $\Delta V$ is very small, and in a lot of cases may be neglected (under lab conditions, $V_m \Delta p$ is small!)

Hence, we can normally assume that Gibbs energies for solids and liquids are independent of pressure - however, for geophysical problems which involve very high temperatures and pressures, the volume effect on Gibbs energies cannot be ignored!

Suppose that for a solid phase transition that $\Delta_{\text{trs}}V = 1.0 \text{ cm}^3 \text{ mol}^{-1}$, then at a high pressure of 3.0 Mbar (i.e., 3.0 x $10^6$ bar), Gibbs energy of transition from $\Delta_{\text{trs}} G(1 \text{ bar})$ is calculated as:

\[
\Delta_{\text{trs}} G(3 \text{ Mbar}) = \Delta_{\text{trs}} G(1 \text{ bar}) \times \left( \frac{3.0 \times 10^6 \text{ Pa}}{1.0 \times 10^5 \text{ Pa}} \right) \\
= \Delta_{\text{trs}} G(1 \text{ bar}) \times 3.0 \times 10^2 \text{ kJ mol}^{-1}
\]

### Gases

Molar volumes of gases are very large, so Gibbs energy may be strongly dependent upon the pressure

\[
\Delta G_\text{pf}(p_f) - \Delta G_\text{pi}(p_i) = \int_{p_i}^{p_f} \frac{RT}{p} dp
\]

If pressure is increased by 10x at room temperature, then molar Gibbs energy increases by about a factor of 6 kJ mol$^{-1}$.

As well, if we set $p = p_o$ (standard pressure of 1.0 bar), the molar Gibbs energy of perfect gas at some pressure $p$ is related to its standard value by

\[
\Delta G_\text{pf}(p) = G_\text{pf}^0 + RT \ln \left( \frac{p}{p_o} \right)
\]
Chemical Potential

Chemical potential, \( \mu \), of a pure substance is defined as

\[
\mu = \left( \frac{\partial G}{\partial n} \right)_{T, p}
\]

Chemical potential is useful for demonstrating how the Gibbs energy of a system changes as a substance is added to it. For a pure substance,

\[
\mu = G_m
\]

Here, the chemical potential is the same as the molar Gibbs energy. For example, chemical potential of a perfect gas can be rewritten as

\[
\mu = \mu^\oplus + RT \ln \left( \frac{p}{p^\oplus} \right)
\]

We give it a special name because later we will apply it to mixtures and talk about the chemical potentials of individual components. However, remember that the chemical potential of some compound is just its molar Gibbs free energy.

Real Gases & Fugacity

Consider the pressure dependence of the chemical potential of a real gas

To adapt to the case of a real gas, we replace the true pressure \( p \) by an effective pressure \( f \), called the fugacity

\[
\mu = \mu^\oplus + RT \ln \left( \frac{f}{p} \right)
\]

Fugacity, from Latin for “fleetness”; refers to the “tendency to escape”. Fugacity has the same units as pressure, and is a bit of a “fudge factor” for treating real gases

In physical chemistry, since many properties of materials are derived from chemical potentials, fugacities are used to describe pressures

As \( p \to 0 \), \( \mu \) coincides with a perfect gas. At intermediate \( p \), attractive forces dominate (\( f < p \)), and at high pressures, repulsion gives \( f > p \)

Standard States of Real Gases

A perfect gas is in standard state when pressure is \( p^\oplus = 1 \text{ bar} \): pressure arises from kinetic energy, with no interactions taken into account

The standard state of a real gas is a hypothetical state in which the gas is at \( p^\oplus \) and behaving perfectly

We choose a hypothetical standard state in order to standardize the interactions between gas particles (for different types of gases) by setting all interactions to zero. We do not choose the standard state as a gas at pressure approaching zero, since the chemical potential of a gas will approach negative infinity at this point: \( (\mu \to -\infty \text{ as } p \to 0) \)

Standard chemical potential of gases, \( \mu^\oplus \), arises solely from internal molecular structure and properties of gases, and not from the interactions between particles
Fugacity vs. Pressure

Fugacity is written as:

\[ f = \phi \theta \]

where \( \phi \) is the dimensionless fugacity coefficient, which depends on the nature of the gas, the temperature and the pressure. Thus,

\[ \mu = \mu^\circ + RT \ln \left( \frac{p}{p^\circ} \right) + RT \ln \phi \]

where \( \mu^\circ \) refers to the standard state gas influenced only by kinetic energy. The second term describes the perfect gas, and \( RT \ln \phi \) expresses the effect of the molecular forces of a real gas: all gases become perfect as \( p \) approaches 0, so \( f \) → \( p \) as \( p \) → 0, and \( \phi \) → 1 as \( p \) → 0.

We can prove that the fugacity coefficient of a gas can be calculated from

\[ \ln \phi = \int_0^p \left( \frac{Z - 1}{p} \right) dp \]

where \( Z = \frac{pV}{nRT} \) is the compression factor of the gas. Let's do this on the next slide:

Fugacity and Compression Factor, \( Z \)

For all gases

\[ G_u(p) - G_u(p') = \int_{p'}^p V_{m} dp = \mu - \mu' = RT \ln \left( \frac{p'}{p} \right) \]

\( f' \) is fugacity at pressure \( p' \) and \( f \) is fugacity at pressure \( p \). Perfect gas:

\[ \int_{p'}^p V_{m} dp = \mu_{\text{perfect}} - \mu'_{\text{perfect}} = RT \ln \left( \frac{p}{p'} \right) \]

the difference of the equations is

\[ \int_{p'}^p (V_{m} - V_{m, \text{perfect}}) dp = RT \ln \left( \frac{Z}{Z'} \right) - \ln \left( \frac{p}{p'} \right) \]

which is rearranged to:

\[ \ln \left( \frac{Z}{Z'} \right) = -\frac{1}{RT} \int_{p'}^p (V_{m} - V_{m, \text{perfect}}) dp \]

If \( p' \to 0 \), the gas behaves perfectly, and \( f' \to p' \).

\[ \ln \left( \frac{Z}{Z'} \right) = -\frac{1}{RT} \int_{p'}^p (V_{m} - V_{m, \text{perfect}}) dp \]

\( V_{m, \text{perfect}} = \frac{RT}{p} \), \( V_m = \frac{RTZ}{p} \), and substituting in gives us proof, \( \text{q.e.d.} \).

Fugacity and van der Waals Gases

To evaluate \( \phi \), experimental data on \( Z \) is needed from low pressures up to the pressure of interest - sometimes, the fugacity can be obtained from the virial coefficients of a gas:

\[ \ln \phi = \phi' = \frac{1}{2} C_2 p^2 + \ldots \]

The full vdW equations of state are shown in terms of fugacity coefficients as functions of reduced pressure (and labeled as curves at reduced temperatures, \( T/ T_c \)), providing estimates of fugacities for a wide range of gases.

Fugacity Summary

Most gases:

\( Z < 1 \) at moderate pressures, attractive forces
\( Z > 1 \) at high pressures, repulsive forces

\( Z < 1 \), moderate \( p \)
\[ \ln \phi = \int_0^p \left( \frac{Z - 1}{p} \right) dp < 0 \]
\( f < p \)
\( \mu < \mu^\circ \)
particles stick together

\( Z > 1 \), high \( p \)
\[ \ln \phi = \int_0^p \left( \frac{Z - 1}{p} \right) dp > 0 \]
\( f > p \)
\( \mu > \mu^\circ \)
particles driven apart
Suppose attractive interactions for ammonia gas can be neglected at 10.00 atm and 298.15 K. Find an expression for fugacity of a van der Waals gas in terms of the pressure.

We neglect \( a \) from the VdW equation (for attractive forces) and write

\[
p = \frac{RT}{Z-1} \quad Z = 1 + \frac{b}{RT}
\]

Evaluating the integral for \( \ln \phi \):

\[
\ln \phi = \int \left( \frac{Z - 1}{p} \right) dp = \int \left( \frac{b}{RT} \right) dp = \frac{bp}{RT}
\]

Then solving for \( f \) we have

\[
\phi = \frac{f}{p} = e^{\frac{bp}{RT}} \quad f = pe^{\frac{bp}{RT}}
\]

with \( b = 3.707 \times 10^{-2} \text{ L mol}^{-1} \), then by \( RT = 1.515 \times 10^{2} \), giving

\[
f = (10.00 \text{ atm}) \times \exp(0.01515) = 10.2 \text{ atm}
\]

The repulsive term, \( b \), increases the fugacity above the pressure, so the "escaping tendency" is greater than if it were perfect.