
The Second Law: The Machinery

Chapter 5 of Atkins: The Second Law: The Concepts

Sections 5.1-5.6, 6th Ed.; 5.1 - 5.5, 7th Ed.; 3.7-3.9 8th, 9th Eds.

Combining First and Second Laws

Properties of the Internal Energy

Properties of the Gibbs Energy

The Chemical Potential of a Pure Substance

Real Gases: The Fugacity

Definition of Fugacity

Standard States of Gases

Relation Between Fugacity and Pressure

The Second Law: The Machinery

The laws of thermodynamics we have learned thus far now enable us to begin finding relationships between properties that may have not been thought to be related with one another - there are many interesting “hidden” relationships that can be extracted - lets now *combine the laws*:

The First Law of Thermodynamics:

$$dU = dq + dw$$

For reversible change in constant composition system with no non-expansion work

$$dw_{\text{rev}} = -p dV \quad dq_{\text{rev}} = T dS$$

Therefore:

$$dU = T dS - p dV$$

**Fundamental
Equation**

dU is an exact differential, independent of path, so the same values for dU are obtained regardless of change being reversible or irreversible (closed system, no non-expansion work)

Properties of Internal Energy †

Reversible change: $T dS$ same as dq , and $-p dV$ same as dw

Irreversible change: $T dS > dq$ (Clausius inequality), and $-p dV > dw$

For a system of constant composition: $dw + dq = T dS + -p dV$

When S and V are changed, $dU \propto dS$ and $dU \propto dV$, from the fundamental equation, suggesting that dU should be written as a function of S and V

$$dU = T dS - p dV$$

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

The equation above means that the change in U is proportional to changes in S and V , with the coefficients being slopes of plots of U against S at constant V , and U against V at constant S . For systems of constant composition:

Thermodynamic definition of temperature $\longrightarrow \left(\frac{\partial U}{\partial S} \right)_V = T$ $\left(\frac{\partial U}{\partial V} \right)_S = -p$ \longleftarrow Thermodynamic definition of pressure

Maxwell Relations

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

$$df = g dx + h dy \text{ is exact if } \left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y$$

We know that $dU = T dS - p dV$ is exact, then

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

We have generated a relationship between quantities that would not seem to be related on first sight! In fact, the four **Maxwell relations** can be derived from the four state functions U , H , G and A :

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

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

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

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Variation of Internal Energy with Volume

In Chapter 3, we defined a coefficient called the internal pressure

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$$

which can be written as a **thermodynamic equation of state**, in terms of p and T , and can therefore be applied to any substance

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

This expression for π_T is obtained by dividing by dV and substituting in:

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

$$\left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{\partial U}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_T + \left(\frac{\partial U}{\partial V} \right)_S$$

a Maxwell relation

$$= T \left(\frac{\partial S}{\partial V} \right)_T - p \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

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 ΔG , this results from changes in H , S and T . Again, for infinitesimal changes:

$$dG = dH - TdS - SdT$$

Since $H = U + pV$: $dH = dU + pdV + Vdp$

For a closed system doing no non-expansion work, dU can be replaced by the fundamental equation, $dU = TdS - pdV$

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

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 and we do not have to worry about ΔS_{univ} to determine spontaneity!***

Gibbs Energy, Pressure & Temperature

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

$$dG = Vdp - SdT$$

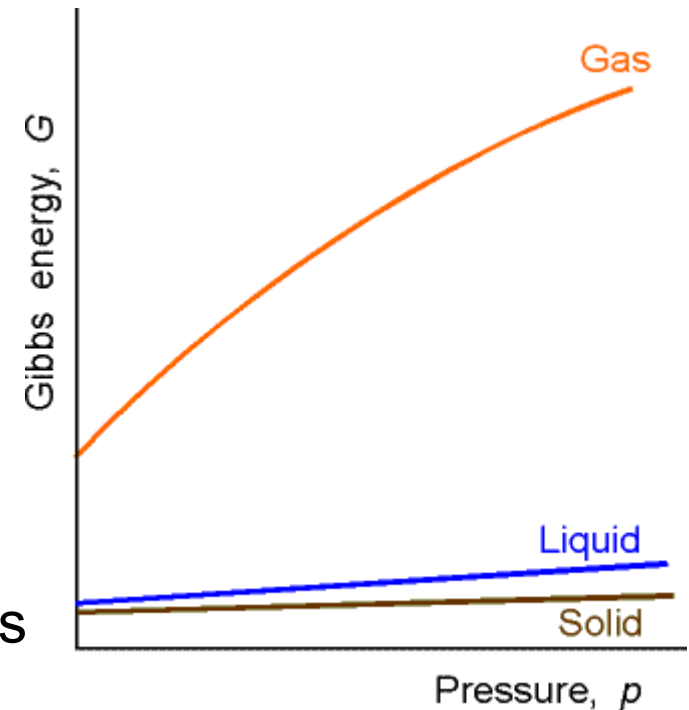
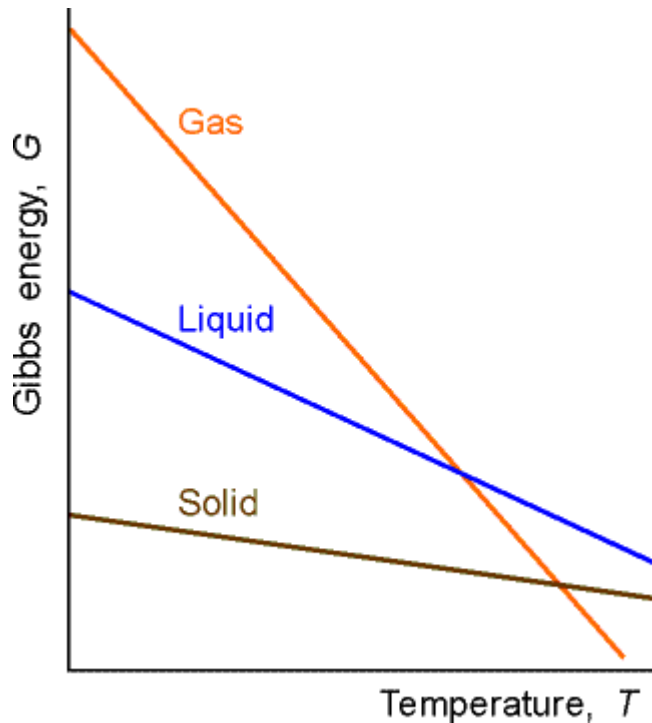
$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

G decreases when the T is increased at constant p , because S is positive

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

G decreases most sharply when S is large (G of gaseous phase is more sensitive to ΔT than liquids or solids)

G increases when p is increased at constant T (since V is positive)



Temperature Dependence of G

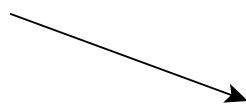
In many chemical and physical transformations, the **equilibrium composition** of a system depends on the Gibbs energy - so we must know the response of the Gibbs energy to temperature changes

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

and we can rearrange to $\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$

The LHS can be shown to be the derivative of G/T wrt T : $\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\frac{d}{dT}\frac{1}{T}$

(in 59-241, you will see that we want the Gibbs-Helmholz equation in this form, since the equilibrium constants of reactions are related to G/T rather than just G)



from which follows the **Gibbs-Helmholz equation** (which relates G and H):

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

Pressure Dependence of G

Calculate the ΔG_m of (a) H_2O (l) treated as an **incompressible fluid**, and (b) H_2O treated as a **perfect gas**, when **pressure is increased isothermally** from 1.0 bar to 2.0 bar at 298 K

Integrate $dG = Vdp - SdT$ wrt p at constant T

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

(a) **incompressible fluid**, $V_m = \text{constant}$, (b) **perfect gas**, $V_m = RT/p$

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

$$= (18.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times (1.0 \times 10^5 \text{ Pa}) = \boxed{+1.8 \text{ J mol}^{-1}}$$

$$(b) \quad G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} \frac{RT}{p} dp = RT \ln \left(\frac{p_f}{p_i} \right)$$

$$= (2.48 \text{ kJ mol}^{-1}) \times \ln(2.0) = \boxed{+1.7 \text{ kJ mol}^{-1}}$$

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

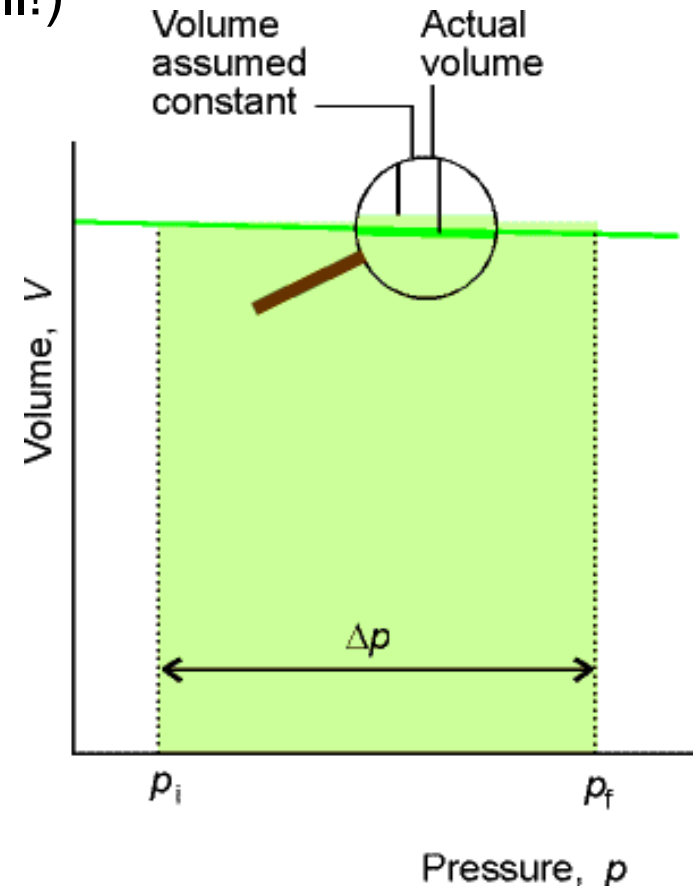
Pressure Dependence of G , Solid & Liquid

For liquids and solids ΔV 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., $3.0 \times 10^6 \text{ bar}$), Gibbs energy of transition from $\Delta_{\text{trs}} G (1 \text{ bar})$ is calculated as:

$$\begin{aligned} \Delta_{\text{trs}} G (3 \text{ Mbar}) &= \Delta_{\text{trs}} G (1 \text{ bar}) + \Delta V_m (p_f - p_i) \\ &= \Delta_{\text{trs}} G (1 \text{ bar}) + (1.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times (3.0 \times 10^{11} \text{ Pa} - 1.0 \times 10^5 \text{ Pa}) \\ &= \Delta_{\text{trs}} G (1 \text{ bar}) + (3.0 \times 10^2 \text{ kJ mol}^{-1}) \end{aligned}$$



Pressure Dependence of G , Gases

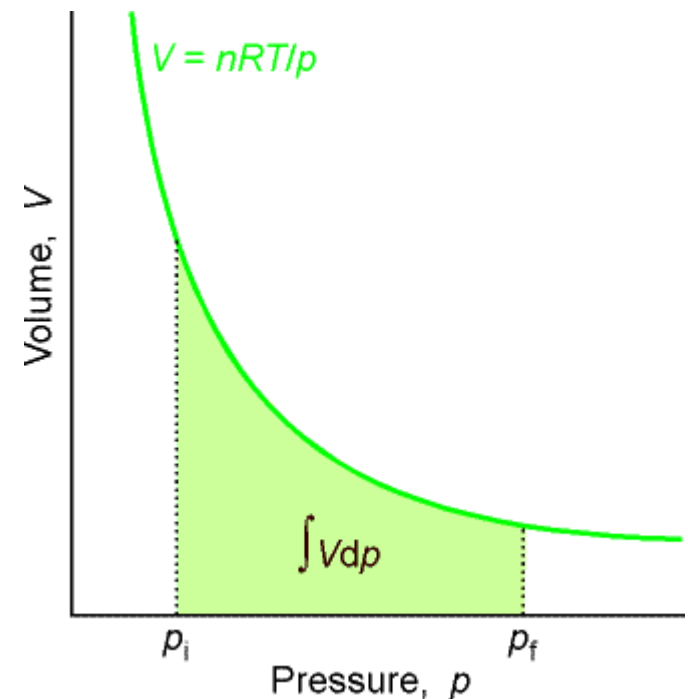
Molar volumes of gases are very large, so Gibbs energy may be strongly dependent upon the **pressure**

$$G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} \frac{RT}{p} dp = RT \ln \left(\frac{p_f}{p_i} \right)$$

If pressure is increased by $10\times$ at room temperature, then molar Gibbs energy increases by about a factor of 10.

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

$$G_m(p) = G_m^\circ + RT \ln \left(\frac{p}{p^\circ} \right)$$



Chemical Potential

Chemical potential, μ , 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, Gibbs energy is $G = n \times G_m$, so

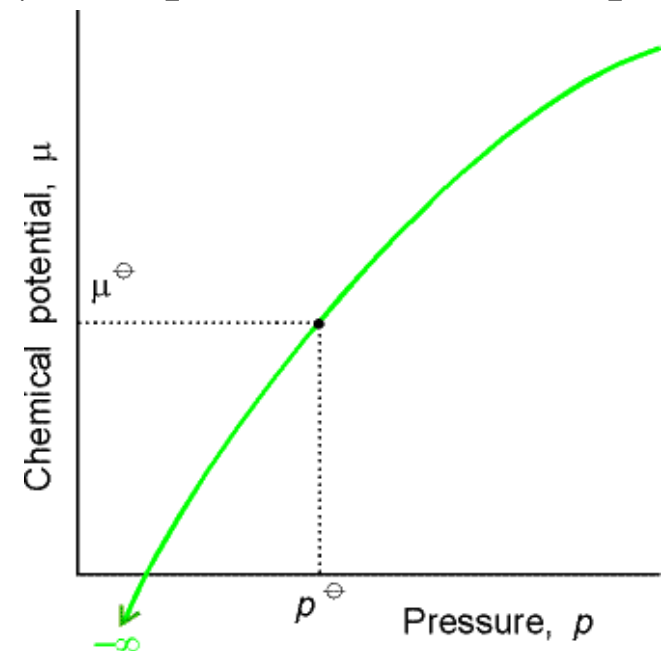
$$\mu = \left(\frac{\partial n G_m}{\partial n} \right)_{T,p} = G_m$$

Here, the **chemical potential is the same as the molar Gibbs energy**. For example, chemical potential of a perfect gas is:

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

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.*

$\mu \propto \ln p$, standard state at p°



Chemical Potential

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

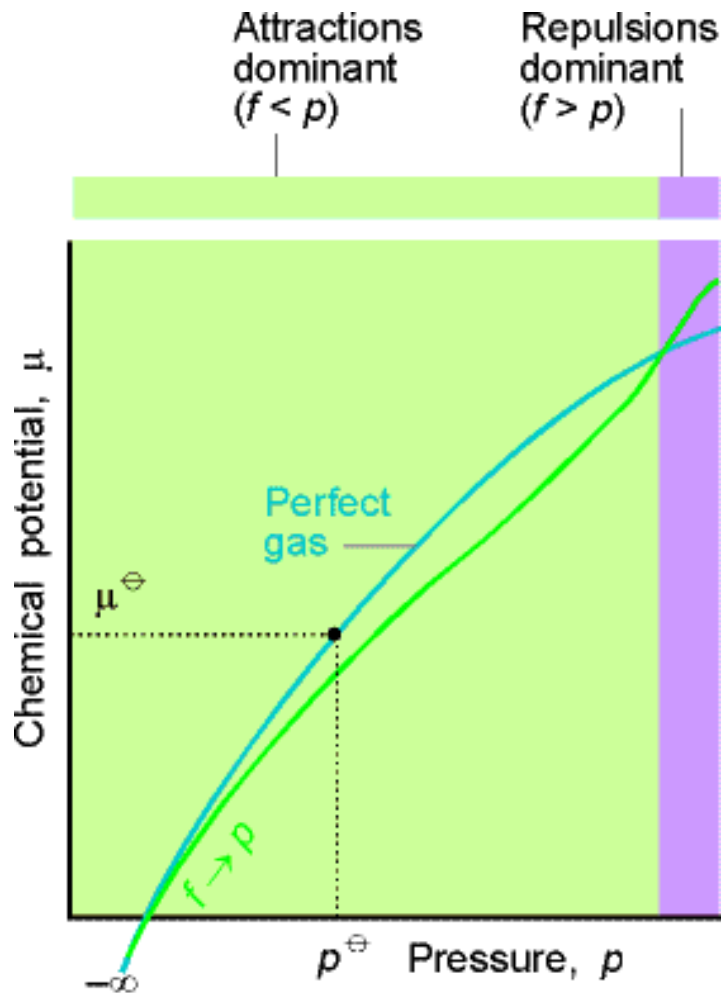
This equation you will use about a hundred times in the next month, so make sure you understand it.

It simply says that we can define a molar free energy for any substance as just the molar free energy under standard conditions plus some term that depends on the temperature and the natural log of the relative amount of the substance (expressed as a **pressure** in the case of a gas or a **concentration** in the case of a solute in a liquid).

For an ideal gas, the chemical potential at some pressure is just the chemical potential at the standard pressure plus the change in entropy associated with changing to the new pressure. In general, contributions to chemical potential are split into **(i)** terms that are properties of the molecules in question and **(ii)** terms that have to do with changing the total number of states that are available to the molecules.

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**

$$\mu = \mu^\ominus + RT \ln \left(\frac{f}{p^\ominus} \right)$$

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 $p \rightarrow 0$, μ 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° (1 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° 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: ($\mu \rightarrow -\infty$ as $p \rightarrow 0$)
- **Standard chemical potential** of gases, μ° , arises solely from internal molecular structure and properties of gases, and not from the interactions between particles

Fugacity vs. Pressure

Fugacity is written as: $f = \phi p$

where ϕ 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 μ° refers to the standard state gas influenced only by kinetic energy

The **second term** describes the perfect gas, and the **third term** expresses the effect of the molecular forces of a real gas: all gases become perfect as p approaches 0, so $f \rightarrow p$ as $p \rightarrow 0$, and $\phi \rightarrow 1$ as $p \rightarrow 0$

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 $Z = pV/nRT = pV_m/RT$ is the compression factor of the gas. Let's do this on the next slide:

Fugacity and Compression Factor, Z

For all gases

$$G_m(p) - G_m(p') = \int_{p'}^p V_m dp = \mu - \mu' = RT \ln \left(\frac{f}{f'} \right)$$

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

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

the difference of the equations is

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

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

If $p' \rightarrow 0$, the gas behaves perfectly, and $f' \rightarrow p'$

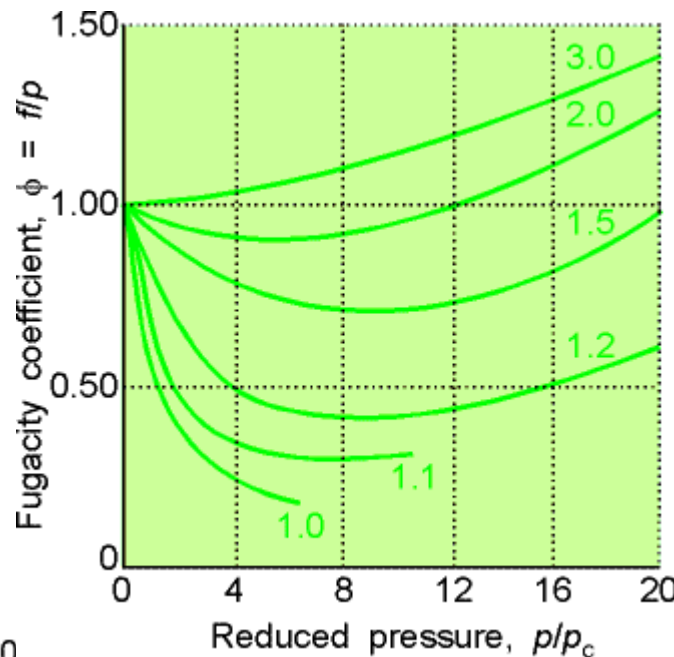
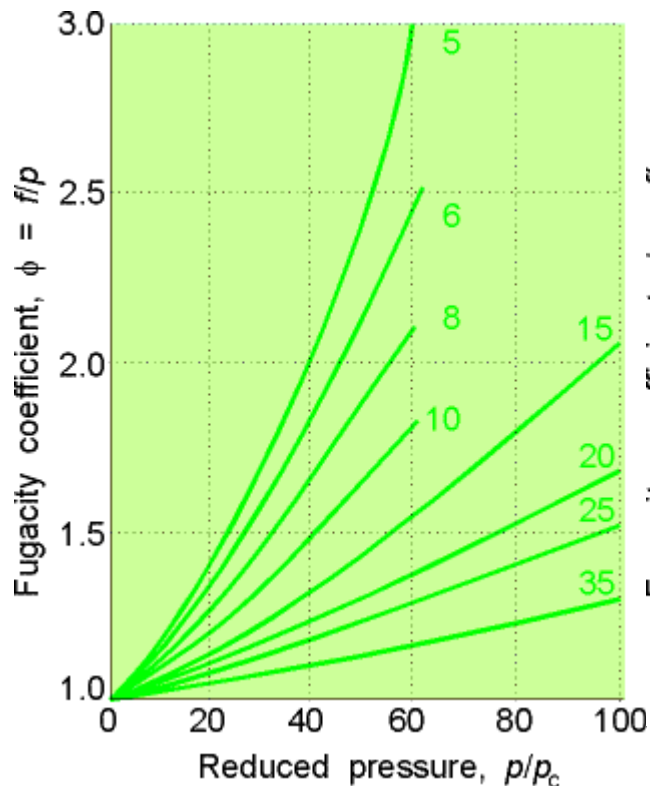
$$\ln \left(\frac{f}{p} \right) = \ln \phi = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect,m}}) dp$$

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

Fugacity and van der Waals Gases

To evaluate ϕ , 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:

$$\ln \phi = B'p + \frac{1}{2} C'p^2 + \dots$$



The full VdW equations of state are shown in terms of fugacity coefficients as functions of reduced pressure (and labelled 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 higher 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
“escape tendency” lessened

$Z > 1$, high p

$$\ln \phi = \int_0^p \left(\frac{Z - 1}{p} \right) dp > 0$$

$$f > p$$

$$\mu > \mu^\circ$$

particles driven apart
“escape tendency” heightened

Fugacity Calculation

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

$$p = \frac{RT}{V_m - b}, \quad Z = 1 + \frac{bp}{RT}$$

Evaluating the integral for $\ln \phi$:

$$\int_0^p \left(\frac{Z - 1}{p} \right) dp = \int_0^p \left(\frac{b}{RT} \right) dp = \frac{bp}{RT}$$

Then solving for f we have

$$f = p e^{bp/RT}$$

with $b = 3.707 \times 10^{-2} \text{ L mol}^{-1}$, then $pb/RT = 1.515 \times 10^{-2}$, giving

$$f = (10.00 \text{ atm}) \times e^{0.01515} = 10.2 \text{ atm}$$

The repulsive term, b , increases the fugacity above the pressure, so the “escaping tendency” is greater than if it were perfect