A DEEPER LOOK 2 The fugacity

At various stages in the development of physical chemistry it is necessary to switch from a consideration of idealized systems to real systems. In many cases it is desirable to preserve the form of the expressions that have been derived for an idealized system. Then deviations from the idealized behaviour can be expressed most simply. For instance, the pressure-dependence of the molar Gibbs energy of a perfect gas is

$$G_m = G_m^{\ominus} + RT \ln\left(\frac{p}{p^{\ominus}}\right) \tag{1a}$$

For a real gas, the true pressure, p, is replaced by an effective pressure, called the **fugacity**,[1] f, to give

$$G_m = G_m^{\ominus} + RT \ln\left(\frac{f}{p^{\ominus}}\right) \tag{1b}$$

The fugacity, a function of the pressure and temperature, is defined so that this relation is exactly true. A very similar approach is taken in the discussion of real solutions where 'activities' are effective concentrations, so $f/p^{\ominus}$ may be regarded as a gas-phase activity.

Although thermodynamic expressions in terms of fugacities derived from this expression are exact, they are useful only if fugacities can be expressed in terms of actual pressures. To develop this relation the fugacity is written as

$$f = \phi p \tag{2}$$

where ϕ is the dimensionless **fugacity coefficient**, which in general depends on the temperature, the pressure, and the identity of the gas. For a perfect gas, $\phi = 1$ at all temperatures and pressures.

The starting point for establishing the relation between the fugacity coefficient and the pressure of a gas is the general relation that, at constant temperature,

$$dG_m = V_m dp \tag{3a}$$

and its integral form

$$G_m(p_2) - G_m(p_1) = \int_{p_1}^{p_2} V_m \, dp \tag{3b}$$

Step 1 *Express the molar Gibbs energies in terms of fugacity*
From the definition in eqn 1b,

$$G_m(p_2) - G_m(p_1) = \left\{ G_m^{\ominus} + RT \ln\frac{f_2}{p^{\ominus}} \right\} - \left\{ G_m^{\ominus} + RT \ln\frac{f_1}{p^{\ominus}} \right\}$$
$$= RT \ln\frac{f_2}{f_1}$$

In this expression, f_1 is the fugacity when the pressure is p_1 and f_2 is the fugacity when the pressure is p_2. That is, from eqn 3b,

$$\int_{p_1}^{p_2} V_m \, dp = RT \ln\frac{f_2}{f_1} \tag{4a}$$

For a perfect gas,

$$\int_{p_1}^{p_2} V_{perfect,m} \, dp = RT \ln\frac{p_2}{p_1} \tag{4b}$$

Step 2 *Express the integral in terms of the difference of molar volumes of real and perfect gases*
The difference between the real and perfect expressions is

$$\int_{p_1}^{p_2} (V_m - V_{perfect,m}) \, dp = RT\left(\ln\frac{f_2}{f_1} - \ln\frac{p_2}{p_1} \right) = RT \ln\frac{f_2/p_2}{f_1/p_1}$$

which can be rearranged into

$$\ln\frac{f_2/p_2}{f_1/p_1} = \frac{1}{RT} \int_{p_1}^{p_2} (V_m - V_{perfect,m}) \, dp \tag{5}$$

Step 3 *Allow one of the pressures to approach zero*
When $p_1 \to 0$, the gas behaves perfectly and f_1 becomes equal to the pressure, p_1. Therefore, $f_1/p_1 \to 1$ as $p_1 \to 0$. On taking this limit, which means setting $f_1/p_1 = 1$ on the left of eqn 5 and $p_1 = 0$ on the right, eqn 5 becomes

$$\ln\frac{f_2}{p_2} = \frac{1}{RT} \int_0^{p_2} (V_m - V_{perfect,m}) \, dp \tag{6}$$

At this stage the subscript 2 may be dropped (so that p_2 becomes p, the pressure of interest, and f_2 becomes f, the fugacity at that pressure), and with $\phi = f/p$,

$$\ln\phi = \frac{1}{RT} \int_0^{p} (V_m - V_{perfect,m}) \, dp \tag{7}$$

For a perfect gas, $V_{perfect,m} = RT/p$. For a real gas, $V_m = RTZ/p$, where Z is the compression factor of the gas. With these two substitutions, eqn 7 becomes

$$\ln\phi = \int_0^{p} \frac{Z-1}{p} \, dp \tag{8}$$

Provided it is known how Z varies with pressure up to the pressure of interest, this expression can be used to determine the fugacity coefficient and hence, through eqn 2, the fugacity of the gas at the pressure interest.

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[1] The name 'fugacity' comes from the Latin for 'fleetness' in the sense of 'escaping tendency'; fugacity has the same dimensions as pressure.

Step 4 *Analyse the implications of the equation*

For a perfect gas, $\phi = 1$ at all pressures and temperatures. For most gases $Z < 1$ up to moderate pressures, but $Z > 1$ at higher pressures. If $Z < 1$ throughout the range of integration, then the integrand in eqn 8 is negative and $\phi < 1$. This value implies that $f < p$ (the molecules tend to stick together) and that 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, $\phi > 1$, and $f > p$ (the repulsive interactions are dominant and tend to drive the particles apart). Now the molar Gibbs energy of the gas is greater than that of the perfect gas at the same pressure.

Figure 1, which has been calculated using the full van der Waals equation of state, shows how the fugacity coefficient depends on the pressure in terms of the reduced variables.
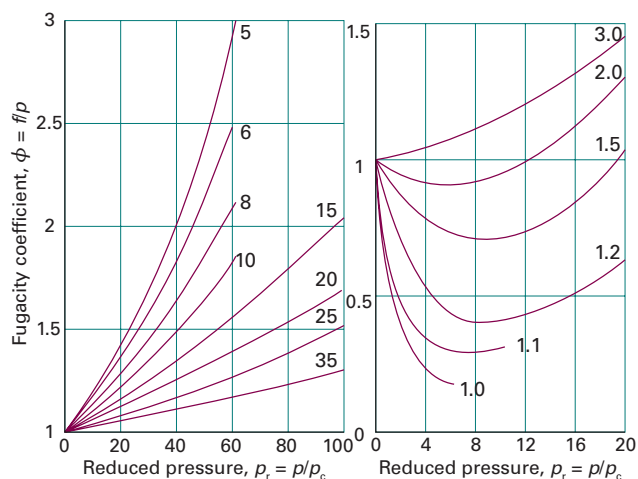
Figure 1 The fugacity coefficient of a van der Waals gas plotted using the reduced variables of the gas. The curves are labelled with the reduced temperature $T_r = T/T_c$.