Excess functions are introduced in Thermodynamics to modify simple models of substance behaviour (ideal gas model, ideal mixture model, ideal solution model), to account for deviations shown in real substances. They were first introduced by the American Gilbert Lewis in 1907 as a difference between ideal partial pressures and real 'activities' or 'fugacities', as he named them.

**MATHEMATICAL EXPLANATION**

Some functions of interest, say \( y(x) \), may vary slowly and it is then advantageous to put it as a simple function (e.g. a straight line) plus a deviation. The most common case is the local expansion of the function as the tangent line at a given point of interest, \( x_0 \), plus its deviation (Fig. 1):

\[
y(x) = y(x_0) + y'(x_0)(x-x_0) + \eta(x)
\]

function = ref.value + local slope + real difference

In many thermodynamic functions, however, the interest is not in a local expansion but in an asymptotic expansion (Fig. 1), because the simple models only approach real behaviour in the limit (e.g. when the pressure is very low, \( p \to 0 \), or when the concentration is very low, \( x_i \to 0 \)). A similar expansion to (1), \( y(x) = y(x_\infty) + y'(x_\infty)(x-x_\infty) + \eta(x) \) is no longer valid since \( y(x_\infty) \) is ill-defined. Sometimes even \( y'(x_\infty) \) is ill-defined, but this may be circumvented by changing the variables (e.g. from \( p \) to \( \ln p \), as for the molar volume versus pressure, \( v(p) \), that \( v_{p=0}\to\infty, \frac{dv}{dp}_{p=0}\to\infty, \) but \( \frac{dlnv}{dlnp}_{p=0}=1 \). The problem of the asymptotic-base-point being inaccessible is solved by choosing an ideal-base-point not belonging to the function but to the asymptotic model near the range of practical interest, i.e. point \( y_\infty(x_0) \) in Fig. 1, and, instead of \( y(x) = y(x_\infty) + y'(x_\infty)(x-x_\infty) + \eta(x) \) use:

\[
y(x) = y_\infty(x_0) + y'_\infty(x_0)(x-x_0) + \eta(x)
\]

function = ideal ref.value + ideal slope + real difference (\( \equiv \text{excess} \))

i.e. excess function \( \equiv \text{real function} - \text{ideal function} \)
Excess functions

Fig. 1. Illustration of a local and an asymptotic expansion of a function. Notice the difference between $y_{\infty}(x_0)$ and $y(x_0)$ in the asymptotic expansion.

**Physical example: Molar volume of a pure substance**

The molar volume of a pure substance, $v \equiv V/n$, related to the density by $v = M/\rho$, is a function of $T$ and $p$ for a given substance. There is no asymptotic behaviour with temperature of interest in this case (but the limit $T \to 0$ is important in Third Law related matters), but there is indeed an interest to expand the variation with pressure relative to the ideal gas model $v = RT/p$.

Introducing $Z \equiv pv/(RT)$ and changing variables from $v(p)$ to $\ln(vp)$, the expansion is then $\ln v = \ln(RT) - \ln p + \ln Z$, or, to be more physical, $\ln v = \ln(T_{0}/p_{0}) - \ln(p/p_{0}) + \ln(Z/Z_{0})$, where $T_{0}$, $p_{0}$ and $v_{0}$ are freely chosen to make the function nondimensional (although one usually chooses $v_{0} = RT_{0}/p_{0}$) and $Z_{0}$ is measured. In conclusion:

$$\ln(v/v_{0}) = \ln(T/T_{0}) + (-1)(\ln(p/p_{0}) - \ln(p_{0}/p_{0})) + \ln(Z(T_{0}, p/p_{0}))$$

(3)

function = ideal ref. value + ideal slope + real difference (\textit{equiv excess})

For the case of pure water, if one chooses $T_{0} = 288$ K, $p_{0} = 0.1$ MPa and $v_{0} = RT_{0}/p_{0} = 0.024$ m$^{3}$/mol, the expansion is plotted in Fig. 2, where it is seen that the molar volume jumps to $18 \cdot 10^{-6}$ m$^{3}$/mol after reaching the vapour/liquid phase-change (at 0.0017 MPa for 288 K, $\ln(0.017) = -4$, and at 0.1 MPa for 373 K, $\ln(1) = 0$).

Fig. 2. Expansion of molar volume, $v$, vs. pressure, $p$, for a pure substance at constant temperature: the case of water at 25 °C and 100 °C.
CHEMICAL POTENTIAL FOR A PURE SUBSTANCE

Similar to temperature and pressure being the escaping force for thermal energy ($\int T\text{d}S$) and mechanical energy ($-\int p\text{d}V$), respectively, the chemical potential, $\mu$, is the escaping force for chemical energy ($\int \Sigma \mu_i \text{d}n_i$), i.e. energy associated to the flow of chemical species through a frontier.

Although $\mu_i \equiv -\partial S/\partial n_i|_{U,V,n_j}$, they are not absolute values, as can be seen from $G=\Sigma n_i \mu_i$ ($G$ is an energy function, defined with an arbitrary constant, and for a pure substance $G=n \mu$, thus $\mu$ is defined with an arbitrary constant).

For a pure substance $G=n \mu$ and $\mu=h-Ts$, $\text{d}\mu=-sdT+vdp$, and in the ideal gas limit $v=RT/p$, thus the ideal chemical potential is $\mu(T,p)=\mu^{\ominus}(T,p^{\ominus})+RT\ln(p/p^{\ominus})$, and one chooses the ideal model as (with $\ln(p/p^{\ominus})$ as the independent variable, see Fig. 1):

$$\mu(T,p)/(RT) = \mu^{\ominus}(T,p^{\ominus})/(RT) + \ln(p/p^{\ominus}) + \ln\gamma(T,p)$$

$$\text{function} = \text{ideal ref.value} + \text{ideal slope} + \text{real difference} (=\text{excess})$$

Notice in Fig. 3 that from $dG=-SdT+Vdp+\mu \text{d}n$, $\partial \mu/\partial T=-s$, and that, although once condensed $\partial(\mu/(RT)/\partial p<<1$, it grows exponentially in the $\mu$-ln$p$ plot.

Fig. 3. Expansion of chemical potential, $\mu$, vs. pressure, $p$, for a pure substance at constant temperature: the case of water at 25 °C and 100 °C.

ACTIVITY, ACTIVITY COEFFICIENT AND FUGACITY (PURE SUBSTANCES)

Absolute activity, $\lambda(T,p)$, relative activity, $a(T,p)$, activity coefficient, $\gamma(T,p)$, and fugacity, $f(T,p)$, for pure substances (or fixed composition mixtures) are defined as follows. In general:

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

Notice that both $\gamma$ and $a$ are nondimensional, whereas $f$ has units of a pressure. For the choice of the reference state there are two possibilities: either choose the same reference state, $\mu^{\ominus}(T,p^{\ominus})$, for gaseous states and for condensed states (see Fig. 3), what is useful if phase changes are of interest, or choose a

Excess functions
different reference state for condensed states, the real state at the reference pressure (Fig. 3), $\mu^*(T,p^0)$, what is advantageous if phase changes are not of interest. That is:

For a gas (as above):

$$\mu^{id}(T,p) \equiv \mu^0(T,p^0) + RT \ln \left( \frac{p}{p^0} \right)$$ (6)

i.e. the reference state, $\mu^0$, is chosen as a virtual ideal-gas state at $p^0=100$ kPa (Fig. 3). Activities are computed from measured values of the compressibility factor $Z(T,p)$ as:

$$\ln \left( a(T,p) \right) = \frac{p}{p^0} \int_{p\to0}^p \left[ Z(T,p) - 1 \right] d\ln p \ , \ \ln \gamma = \int_{p\to0}^p \left[ Z(T,p) - 1 \right] d\ln p \ , \ f \equiv \gamma p = ap^0$$ (7)

For a condensed substance one may choose instead:

$$\mu^{id}(T,p) \equiv \mu^*(T,p^0) + \nu(p-p^0) \approx \mu^*(T,p^0)$$ (8)

where the reference state, $\mu^*$, is a the real state at $p^0=100$ kPa (Fig. 3). Activities are computed from measured values of the molar volume $v(T,p)$ as:

$$\ln \left( a(T,p) \right) = \frac{1}{RT} \int_{p^0}^p v \, dp \approx \frac{v(p-p^0)}{RT} \ , \ \ln \gamma = \frac{1}{RT} \int_{p^0}^p (v-v^0) \, dp \approx \frac{(v-v^0)(p-p^0)}{RT}$$ (9)

Notice that for multi-phase equilibrium in pure substances, its chemical potential in the coexisting phases must coincide.

**EXCESS FUNCTIONS FOR OTHER VARIABLES (PURE SUBSTANCES)**

Table 1. Expansion for pure substances in terms of the ideal gas model: $Z(T,p)$ and $c_p(T,p\to0)$.

<table>
<thead>
<tr>
<th>Function</th>
<th>Ideal ref. value</th>
<th>Ideal slope</th>
<th>Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$</td>
<td>1</td>
<td>0</td>
<td>+ Z</td>
</tr>
<tr>
<td>$\ln(v/v_0)$</td>
<td>$\ln(T/T_0)$</td>
<td>+ $(-1)\ln(p/p_0)$</td>
<td>$\ln Z$</td>
</tr>
<tr>
<td>$u$</td>
<td>$u_0+c_p,dT$</td>
<td>+ 0</td>
<td>+ $-RT^2\hat{Z}_T\ln p-RT(Z-1)$</td>
</tr>
<tr>
<td>$h$</td>
<td>$h_0+c_p,dT$</td>
<td>+ 0</td>
<td>+ $-RT^2\hat{Z}_T\ln p$</td>
</tr>
<tr>
<td>$s$</td>
<td>$s_0+c_p(T),dT$</td>
<td>+ $(-1)R\ln(p/p_0)$</td>
<td>+ $-R\hat{Z}_T(T-1)$</td>
</tr>
<tr>
<td>$g(\equiv \mu)$</td>
<td>$g^0(T,p_0)$</td>
<td>+ $RT\ln(p/p_0)$</td>
<td>+ $RT\hat{Z}_T(T-1)$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$\mu^0(T,p_0)$</td>
<td>+ $RT\ln(p/p_0)$</td>
<td>$RT\hat{Z}_T(T-1)$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$1/T$</td>
<td>+ 0</td>
<td>+ $Z\hat{Z}/Z$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>1</td>
<td>+ 0</td>
<td>+ $-p\hat{Z}/Z$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>$c_p(T,p\to0)$</td>
<td>+ 0</td>
<td>+ $-RT\hat{Z}<em>T+T\hat{Z}</em>{TT}$</td>
</tr>
<tr>
<td>$\ln(f/p)$</td>
<td>1</td>
<td>+ 0</td>
<td>+ $f(Z-1)$</td>
</tr>
<tr>
<td>$lna$</td>
<td>1</td>
<td>+ 0</td>
<td>+ $f(Z-1)$</td>
</tr>
</tbody>
</table>

Notice that $u_0$ and $h_0$ are related by $h_0=u_0+p_0v_0$. $Z_T=\partial Z/\partial T|_p$. All integrals extend from $p\to0$ to $p$. 

Excess functions 4
All excess functions may be expressed in terms of $f$ or $a$ (e.g. $h - h^\text{id} = R \ln(f/p) / \partial(T) |_{p}$, $s - s^\text{id} = -R \ln(f/p) / \partial(T) |_{p}$, $v - v^\text{id} = RT \ln(f/p) / \partial(p) |_{T}$).

**EXCESS FUNCTIONS IN A MIXTURE**

In general:

$$
\mu_i(T, p, x_i) = RT \ln \lambda_i = \mu_i^\text{id}(T, p, x_i) + RT \ln \frac{a_i}{x_i} = \mu_i^\text{id}(T, p, x_i) + RT \ln \left( \frac{f_i}{x_i f_i^*} \right)
$$

(10)

where the ideal mixture refers to Raoult's law for mixtures of gases and for mixtures of liquids, but to Henry's law for liquid solutions, and the reference state is chosen depending on the type of mixture, as follows.

In a mixture of gases, the reference state for a species $i$ is the ideal state of the pure component at the temperature of interest and at a standard pressure (Fig. 4), and activities are defined by:

$$
\mu_i(T, p, x_i, x_j) = \mu_i^\text{b}(T, p^\text{b}, 1, 0) + RT \ln a_i(T, p, x_i, x_j) = \\
= \mu_i^\text{b}(T, p^\text{b}, 1, 0) + RT \ln \frac{p}{p^\text{b}} + RT \ln x_i + RT \ln \gamma(T, p, x_i, x_j)
$$

(11)

and computed from measures of the partial molar volume of species $i$, $v_i = \partial V / \partial n_i |_{T,p,n_j}$ as:

$$
\ln \left( a(T, p, x_i, x_j) \right) = \frac{x_i p}{p^\text{b}} \int_{p \to 0}^{p} \left[ \frac{v_i(T, p, x_i, x_j)}{RT} - \frac{1}{p} \right] dp, \quad f_i^* = \gamma_i x_i f_i^* = a_i f_i^*
$$

(12)

Fig. 4. Expansion of chemical potential, $\mu_i$, vs. partial pressure, $x_i p$, for a gas in a gaseous mixture at constant temperature.

In a mixture of liquids, and for the solvent in a solution, the reference state for a species $i$ is chosen as the real state of the pure component $i$ at the temperature and pressure of interest (Fig. 5), and activities are defined by:

$$
\mu_i(T, p, x_i, x_j) = \mu_i^*(T, p, 1, 0) + RT \ln a_i(T, p, x_i, x_j) = \\
= \mu_i^*(T, p^\text{b}, 1, 0) + v_i^* \left( p - p^\text{b} \right) + RT \ln x_i + RT \ln \gamma(T, p, x_i, x_j)
$$

(13)
(with the pressure term, $v_i^* (p - p^*)$, usually neglected) and computed from measures of the partial molar volume of species $i$ in the gaseous-phase-mixture at equilibrium with the liquid mixture (at the working temperature and the corresponding pressure, since the influence of pressure on liquid properties was shown to be small, see Eq. (9)), plus measures for the pure substance at two-phase equilibrium. For a given species $i$ at a given temperature, for liquid/vapour equilibrium in the mixture $\mu_{i,L} = \mu_{i,L}^0 + RT \ln a_{i,L} = \mu_{i,G} = \mu_{i,G}^0 + RT \ln a_{i,G}$, and for liquid/vapour equilibrium in the pure state $\mu_{i,L}^* = \mu_{i,L}^0 + RT \ln a_{i,L}^* = \mu_{i,G}^* = \mu_{i,G}^0 + RT \ln a_{i,G}^*$, so that the activity in the liquid mixture is:

$$a_{i,L}(T, p, x_i, x_j) = a_{i,G}(T, p_{eq}, x_i, x_j) \frac{a_{i,G}^*(T, p, 1, 0)}{a_{i,G}^*(T, p_{eq}, 1, 0)} \approx \frac{x_i p}{p_i(T)}, \quad f_i \equiv \gamma_i x_i f_i^* = a_i f_i^*$$

(14)

That is, the activity of a liquid $i$ (in a liquid mixture) is measured as the product of molar fraction times pressure, in the gas phase (also known as partial pressure of species $i$), divided by the liquid/vapour-equilibrium pressure at that temperature for that pure species $i$; for ideal liquid mixtures the molar fraction is precisely $x_{i,G} = p_i^*(T)/p$ (Raoult's law) and thus the activity is $a_{i,L} = 1$.

Fig. 5. Expansion of chemical potential vs. molar fraction, for a liquid in a liquid mixture (e.g. ethanol in a water/ethanol solution) at constant temperature, with the reference state at $\mu_i^*$. Also applicable to a solute $i$ in a solvent $s$, with the reference state at $\mu_{i,s}^\infty$ (see below).

**Solutions.** In a liquid mixture of a liquid solvent and solid or gaseous solutes, the reference state for the solvent $s$ is as just described ($\mu_i^*$ in Fig. 5), but for a species $i$ in solution it is the ideal state of the infinitely diluted solution of just this species in that solvent, at the temperature and pressure of interest. The reference state and the corresponding activity may be defined in molar-fraction bases ($\mu_{i,s}^\infty$ in Fig. 5) or in molar-concentration bases ($\mu_{i,s}^\infty$ in Fig. 6) by:

$$\mu_{i,s}(T, p, x_i, x_j, x_c) = \mu_{i,s}^\infty(T, p, 0^+, 1^-, 0) + RT \ln a_{i,s}(T, p, x_i, x_j, x_c) =$$

$$= \mu_{i,s,0}(T, p, 1^-, 0) + RT \ln a_{i,s,0} = \mu_{i,s,0}(T, p, 1^-, 0) + RT \ln x_i + RT \ln \gamma$$

$$= \mu_{i,s,0}(T, p, c_i, 1^-, 0) + RT \ln a_{i,s,0} = \mu_{i,s,0}(T, p, c_i, 1^-, 0) + RT \ln \frac{c_i}{c_i^0} + RT \ln \gamma$$

(15)

(16)

(17)
where subindex \( s \) stands for the solvent (solute are species \( i \)), subindex \( x \) stands for the mole fraction units, and subindex \( c \) stands for molar concentration units. Notice that the amount of species \( i \) in \( \mu^\circ_{i,s} \) is ambiguously represented by the symbol \( 0^\circ \) in (15), but once the magnitude used to measure it is specified, it takes a more explicit form, as in (16) for mole fractions and (17) for mole concentrations. Notice that sometimes \( c_{i0} \) is not explicitly written since it is taken as unity (e.g. 1 mol/m\(^3\), 1 mol/litre, even 1 mol/kg) and its logarithm 'drops' (the activities \( a_i \) are non-dimensional, but their actual value depends on the unit chosen, e.g. for a 10 g/kg sugar solution in water and assuming ideal behaviour, in (16) we have \( a_i=0.01 \cdot 0.018/0.342=0.53 \cdot 10^{-3} \) relative to unit mole fraction, and in (17) we have \( a_i=29 \) relative to 1 mol/m\(^3\).

Activities of non-volatile solutes are computed from activities of the solvent and Gibbs-Duhem equation, that at constant temperature and pressure reads \( 0=n_s d\mu_s+n_i d\mu_{i,s} \), what yields \( 0=x_s d\ln a_s+x_i d\ln a_{i,s} \).

Notice finally that subscripts \( s, x \) and \( c \) are usually dropped in writing (15-17) because ambiguities are rare if the context is well understood.

**Fig. 6. Expansion of the chemical potential \( \mu_{i,s} \) of a solute \( i \) (e.g. sugar, oxygen) in a solvent \( s \) (e.g. water), vs. concentration, \( c_i \), at constant temperature.**

**IONIC SOLUTIONS**

Some solutes (e.g. \( \text{O}_2(\text{g}) \) and saccharose \( \text{C}_{12}\text{H}_{22}\text{O}_{11}(s) \)) dissolve as whole molecules in water, whereas other solutes (e.g. \( \text{HCl}(\text{g}) \) and \( \text{NaCl}(s) \)) dissolve practically fully ionised, splitting in two ions or more (\( \text{CaCl}_2 \) yields 3 ions), so that the activity in the diluted limit varies with \( c_i^2 \) or \( c_i^n \) and not with \( c_i \). As pure ions cannot be isolated (they always form electrically-balanced in pairs, terns or so), activities and activity coefficients cannot be measured for one ion but for the set of ions formed (e.g. \( a_{\text{HCl(aq)}}=m_{\text{H}^+}m_{\text{Cl}^-}\gamma^\pm, a_{\text{CaCl}_2(aq)}=m_{\text{Ca}^2}\gamma^\pm, \) etc.).

**ACTIVITY QUOTIENT**

For a system subjected to a chemical reaction \( 0=\sum v_i M_i \), with the extent of reaction, \( \xi \), and the affinity, \( A \), defined by \( \xi=(n_i-n_{i0})/v_i \) and \( A=-\sum v_i \mu_i \), the Gibbs function of reaction is given by:
\[
g_r = \frac{\partial G}{\partial \xi} \bigg|_{r,p} = -A = \sum v_i \mu_i = \sum v_i \mu_i^*(T, p^\oplus, 1, 0) + \sum v_i RT \ln a_i
\]

(18)

where the effect of the pressure change from \( p^\oplus \) to \( p \) in the liquid phase has been neglected, and the same symbol \( \mu^* \) stands for pure gases, pure liquids, and infinitely-diluted solutions.

**Equilibrium constant**

The so-called equilibrium constant, \( K(T,p) \), and activity quotient, \( Q(a) \), are defined by:

\[
K(T, p^\oplus) = \prod x_i^{v_i} = \exp \left( -\sum \frac{v_i \mu_i^*(T, p^\oplus)}{RT} \right), \quad \text{and} \quad Q(T, p, x_i, x_j) = \prod a_i^{v_i}(T, p, x_i, x_j)
\]

(19)

so that at any state \( g_r = -RT \ln(K/Q) \), and at equilibrium \( (A=0) \):

\[
K(T, p^\oplus) = Q = \prod a_i^{v_i}
\]

\[
K(T, p^\oplus) = \prod \left( \frac{x_i p}{p^\oplus} \right)^{v_i} \quad \text{per mole-fraction unit}
\]

\[
K(T, p^\oplus) = \prod \left( \frac{c_i}{c_{i,0}} \right)^{v_i} \quad \text{per mole-concentration unit}
\]

(20)

The name activity 'quotient' derives from the fact that some of the stoichiometric coefficients in the \( Q \) product are negative (the product is really a quotient of products).