

Notation

symbol	description
m, M	intensive (molar) and extensive property of pure species
m_i, M_i	as above, but specifically for species i
$m^\circ, m^{\text{ig}}, m^{\text{id}}$	reference state, ideal gas, and ideal solution conditions
m^{sat}	saturation (liquid-vapor equilibrium) conditions
$m^\alpha, m^\beta, m^{\text{l}}, m^{\text{v}}$	α, β arbitrary and l, v liquid and vapor phases
$f, \varphi, \hat{f}_i, \hat{\varphi}_i$	fugacity (coefficient) of pure species and of species i in mixture
x_i, y_i	liquid and gas phase mole fraction of species i
P_T	total pressure of mixture
*	a harder exercise

Fugacity in the gas phase

For an ideal gas, and assuming constant T and N , we have

$$d\mu = dg = v dP \iff \mu - \mu^\circ = g - g^\circ = RT \ln \left(\frac{P}{P^\circ} \right). \quad (1)$$

Exercise 1

Prove the above identity.

For non-ideal gases and fluids, we can extend this identity by defining an effective pressure f such that

$$\mu - \mu^{\text{ig}} =: RT \ln \left(\frac{f}{P^{\text{ig}}} \right) = RT \ln \left(\frac{f}{f^{\text{ig}}} \right). \quad (2)$$

We call f the **fugacity**; it is the pressure that an ideal gas with the same chemical potential would have. By construction, $f^{\text{ig}} = P^{\text{ig}}$, and the second equality follows. The pressure P^{ig} is the pressure of the (real) gas; the superscript ig reminds us that we are considering an ideal gas reference state. It is also convenient to define the **fugacity coefficient** φ , satisfying

$$f =: \varphi P^{\text{ig}} \iff \mu - \mu^{\text{ig}} = RT \ln \left(\frac{\varphi P^{\text{ig}}}{P^{\text{ig}}} \right) = RT \ln \varphi. \quad (3)$$

The fugacity coefficient φ contains no new thermodynamics. It simply hides all the complicated intermolecular interactions that real gases possess, and we can interpret it as a measure of a gas's deviation from ideality: the further the fugacity coefficient of a gas diverges from one, the less ideal is the gas. Conversely, if the gas is ideal, $\varphi \equiv 1$.

Exercise 2

Interpret the nature of intermolecular interactions within a gas having (a) $\varphi > 1$ and (b) $\varphi < 1$.

Exercise 3

*Evaluate the fugacity of a van der Waals gas using the definition of fugacity.

Fugacity is a redefined form of the chemical potential, and indeed shares many of its important identities. The most important is the condition for phase equilibria:

$$\mu^\alpha = \mu^\beta \iff f^\alpha = f^\beta. \quad (4)$$

Exercise 4

Prove the above statement by considering the definition of fugacity.

The definition for fugacity in a mixture is analogous to that of the pure species, given by

$$\mu_i - \mu_i^{\text{ig}} =: RT \ln \left(\frac{\hat{f}_i}{P_i^{\text{ig}}} \right) = RT \ln \left(\frac{\hat{f}_i}{y_i P_T^{\text{ig}}} \right) =: RT \ln \hat{\varphi}_i, \quad (5)$$

where we have used the fact that $P_i^{\text{ig}} = y_i P_T^{\text{ig}}$. Note that we use \hat{f}_i instead of f to represent the fugacity of species i in a mixture.

Exercise 5

Rewrite the definition of $\hat{\varphi}_i$ to show that $\hat{f}_i = y_i \hat{\varphi}_i P_T^{\text{ig}}$. Hence prove that

$$\sum_i y_i d \ln \hat{\varphi}_i = 0, \quad (6)$$

starting from the Gibbs-Duhem relation for chemical potential at constant T and P ,

$$\sum_i n_i d\mu_i = 0.$$

Exercise 6

The chemical potential of species i in an ideal-gas mixture is given by

$$\mu_i^{\text{ig}} = g_i + RT \ln y_i.$$

Prove this identity and use it, along with the definition for fugacity in a mixture, to show that

$$\hat{f}_i^{\text{ig}} = y_i f_i^{\text{ig}} = y_i P_T^{\text{ig}}. \quad (7)$$

Exercise 7

Using the identity for the chemical potential of an ideal-gas mixture above, further show that

$$\mu_i - g_i = RT \ln y_i \hat{\varphi}_i. \quad (8)$$

Exercise 8

Show that the fugacity \hat{f}_i is a partial molar property only for an ideal gas mixture.

Fugacity in the liquid phase

We can evaluate the fugacity of pure liquid species i using its saturation pressure as reference:

$$f_i^l(P) = P_i^{\text{sat}} \frac{f_i^v(P_i^{\text{sat}})}{P_i^{\text{sat}}} \frac{f_i^l(P_i^{\text{sat}})}{f_i^v(P_i^{\text{sat}})} \frac{f_i^l(P)}{f_i^l(P_i^{\text{sat}})} = \varphi_i^{\text{sat}} P_i^{\text{sat}} \exp \left(\frac{1}{RT} \int_{P_i^{\text{sat}}}^P V_i^l dP \right). \quad (9)$$

Exercise 9

Prove the above identity by evaluating each fraction independently.

In addition, assuming (or approximating) that the liquid is incompressible, the last term simplifies as

$$\exp\left(\frac{1}{RT} \int_{P_i^{\text{sat}}}^P V_i^l dP\right) = \exp\left(\frac{V_i^l(P - P_i^{\text{sat}})}{RT}\right).$$

Exercise 10

*State and prove the corresponding identity for a binary solution.

In general, however, it is more useful to consider a reference state not tied to saturation conditions. The ideal-gas reference state is the natural choice for fugacity in the gas phase, but what about the liquid phase? The ideal-gas reference state cannot work here, for the existence of the liquid phase itself reveals non-vanishing intermolecular attraction. The next-simplest choice is to consider a reference state in which all intermolecular attraction is of the same strength; this defines an **ideal solution**. By analogy with the chemical potential for the ideal-gas mixture, we thus have

$$\mu_i^{\text{ig}} = g_i^{\text{ig}} + RT \ln y_i \quad \Longleftrightarrow \quad \mu_i^{\text{id}} = g_i + RT \ln x_i. \quad (10)$$

Exercise 11

Justify that $g_i^{\text{id}} = g_i$.

The physics behind this definition is the implicit claim that the entropy of an ideal gas is equivalent to that of an ideal solution. It is difficult to justify such a claim within the framework of macroscopic thermodynamics; in terms of statistical mechanics, however, we note simply that the energy of each microstate is invariant under particle permutation, and hence that the entropy of solution is purely configurational.

Exercise 12

By analogy with the case of gas-phase mixtures, show that for ideal solutions we have

$$\mu_i^{\text{id}} - g_i = RT \ln \left(\frac{\hat{f}_i^{\text{id}}}{f_i} \right), \quad (11)$$

and hence also that

$$\hat{f}_i^{\text{id}} = x_i f_i. \quad (12)$$

Exercise 13

Referring to the previous exercise, prove also that

$$\hat{f}_i^{\text{id}} = x_i f_i \quad \Longleftrightarrow \quad \hat{\varphi}_i^{\text{id}} = \varphi_i. \quad (13)$$

The above exercise provides a necessary condition that ideal solutions must satisfy. A quantitative measure of the deviation from ideality of a real solution is given by the **activity coefficient**

$$\gamma_i := \frac{\hat{f}_i}{x_i f_i}, \quad (14)$$

which also serves to simplify the important identity

$$\mu_i - \mu_i^{\text{id}} = RT \ln \left(\frac{\hat{f}_i}{x_i f_i} \right) = RT \ln \gamma_i. \quad (15)$$

You should have proved and used this identity in Exercise 12.

Exercise 14

Interpret the nature of intermolecular interactions within a solution having (a) $\gamma_i > 1$ and (b) $\gamma_i < 1$.

Exercise 15

By analogy with the case of gas-phase mixtures, show that

$$\mu_i - g_i = RT \ln x_i \gamma_i. \quad (16)$$

Exercise 16

By analogy with the case of gas-phase mixtures, prove that

$$\sum_i x_i d \ln \gamma_i = 0, \quad (17)$$

starting from the Gibbs-Duhem relation for chemical potential at constant T and P ,

$$\sum_i n_i d\mu_i = 0.$$

At this point it is abundantly clear that the fugacity and activity coefficients share many of the same relationships, which we summarize here:

	fugacity coeff. $\hat{\varphi}_i$	activity coeff. γ_i
definition	$\hat{f}_i/y_i P_T^{\text{ig}} = \hat{f}_i/y_i f_i$	$\hat{f}_i/x_i f_i$
ideal	gas mixture, $\varphi_i \equiv 1$	solution, $\gamma_i \equiv 1$
chem. potential	$\mu_i - \mu_i^{\text{ig}} = RT \ln \hat{\varphi}_i$	$\mu_i - \mu_i^{\text{id}} = RT \ln \gamma_i$
chem. potential	$\mu_i - g_i = RT \ln \hat{\varphi}_i y_i$	$\mu_i - g_i = RT \ln \gamma_i x_i$
Gibbs-Duhem	$\sum_i y_i d \ln \hat{\varphi}_i = 0$	$\sum_i x_i d \ln \gamma_i = 0$