

Activity and Activity Coefficient

The chemical potential of a real gas cannot, in general, be expressed simply in terms of its pressure because a real gas deviates from ideal behaviour. Fugacity provides the correction for this non-ideal behaviour. Activity is introduced to express the thermodynamic state of a real gas in a convenient dimensionless form, while the activity coefficient measures the departure of the gas from ideal behaviour.

Activity

For a real gas, the chemical potential is expressed in terms of fugacity as

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

where f is the fugacity of the gas and f° is the fugacity in the chosen standard state. The ratio f/f° is dimensionless and is defined as the **activity** of the gas.

Thus,

$$a = \frac{f}{f^{\circ}}$$

where a is the activity of the gas.

Substituting this definition into the chemical-potential equation gives

$$\mu = \mu^{\circ} + RT \ln a$$

This is the fundamental thermodynamic definition of activity.

Standard State

The standard state must be specified before an activity can be assigned a numerical value. For gases, the standard state is conventionally chosen as an ideal gas at a standard pressure, usually

$$f^{\circ} = P^{\circ} = 1 \text{ bar.}$$

With this choice,

$$a = \frac{f}{P^{\circ}}$$

Since both f and P° have the dimensions of pressure, their ratio is dimensionless.

For a real gas at pressure P , the fugacity is related to pressure through the fugacity coefficient:

$$f = \varphi P.$$

Therefore,

$$a = \frac{\varphi P}{P^{\circ}}.$$

Thus, the activity of a real gas can be written as

$$a = \varphi \frac{P}{P^{\circ}}$$

This expression clearly separates the two factors affecting the thermodynamic state of the gas:

P/P° represents the pressure relative to the standard pressure, while φ accounts for the non-ideal behaviour of the gas.

Activity of an Ideal Gas

For an ideal gas,

$$f = P$$

and therefore

$$\varphi = 1.$$

The activity becomes

$$a = \frac{P}{P^\circ}.$$

Hence, for an ideal gas,

$$a_{\text{ideal}} = \frac{P}{P^\circ}$$

If the pressure is equal to the standard pressure, $P = P^\circ$, then

$$a = 1.$$

Activity of a Real Gas

For a real gas, $f \neq P$, and therefore its activity is not simply P/P° . Using $f = \varphi P$,

$$a = \varphi \frac{P}{P^\circ}$$

Thus, the activity of a real gas contains the correction for non-ideal behaviour through the fugacity coefficient.

At low pressure, $\varphi \rightarrow 1$, so that

$$a \rightarrow \frac{P}{P^\circ}.$$

Therefore, the activity of a real gas approaches the activity of an ideal gas as the pressure approaches zero.

Activity Coefficient

The activity coefficient is introduced to express the deviation of the actual activity from the activity corresponding to the ideal reference behaviour. For a real gas, the activity may be written as

$$a = \varphi \frac{P}{P^\circ}.$$

If the ideal-gas activity at the same pressure is taken as

$$a_{\text{ideal}} = \frac{P}{P^\circ},$$

then the activity coefficient is defined by

$$a = \gamma_g a_{\text{ideal}}.$$

Substituting the expressions for a and a_{ideal} ,

$$\varphi \frac{P}{P^\circ} = \gamma_g \frac{P}{P^\circ}.$$

Therefore,

$$\boxed{\gamma_g = \varphi}$$

Thus, for a pure real gas when the ideal-gas state at the same pressure is used as the reference, the gas-phase activity coefficient is numerically equal to the fugacity coefficient.

Relation Between Activity, Activity Coefficient and Pressure

The activity of a real gas may therefore be expressed in the form

$$\boxed{a = \gamma_g \frac{P}{P^\circ}}$$

and, for the real-gas treatment described above,

$$\gamma_g = \varphi$$

Consequently,

$$a = \varphi \frac{P}{P^\circ}$$

This is the useful relationship connecting pressure, fugacity, fugacity coefficient, activity and activity coefficient for a real gas.

Relation with Chemical Potential

Starting with

$$\mu = \mu^\circ + RT \ln a,$$

and substituting

$$a = \frac{f}{f^\circ},$$

we obtain

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

For $f^\circ = P^\circ$,

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

Using $f = \varphi P$,

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

Using the logarithmic relation $\ln(ab) = \ln a + \ln b$,

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

The term $RT \ln(P/P^\circ)$ is the ideal-gas contribution, whereas $RT \ln \varphi$ represents the correction arising from the non-ideal behaviour of the real gas.

Limiting Behaviour

At sufficiently low pressure, a real gas approaches ideal behaviour. Therefore,

$$\varphi \rightarrow 1.$$

Consequently,

$$\gamma_g \rightarrow 1.$$

The activity then becomes

$$a \rightarrow \frac{P}{P^\circ}.$$

Thus, the activity coefficient approaches unity in the ideal-gas limit. A value different from unity indicates the presence of non-ideal effects.

Physical Significance of the Activity Coefficient

The activity coefficient provides a measure of the deviation of a real gas from ideal behaviour. When

$\gamma_g = 1$, the gas behaves ideally with respect to the chosen reference state. When $\gamma_g < 1$, the fugacity is lower than the pressure, which is generally associated with

attractive intermolecular interactions. When $\gamma_g > 1$, the fugacity is higher than the pressure and repulsive effects are important.

Since, for the present gas-phase treatment,

$$\gamma_g = \varphi,$$

the behaviour of the activity coefficient follows directly from the fugacity coefficient.

Important Relations

Fugacity:

$$f = \varphi P$$

Activity:

$$a = \frac{f}{f^\circ}$$

For $f^\circ = P^\circ$:

$$a = \varphi \frac{P}{P^\circ}$$

Activity coefficient for the gas-phase reference used here:

$$\gamma_g = \varphi$$

Chemical potential:

$$\mu = \mu^\circ + RT \ln a$$

or

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