

LECTURE

12

CY11001
Spring 2018

Real Gas

Reaction Equilibrium



Department of Chemistry
Indian Institute of Technology
Kharagpur

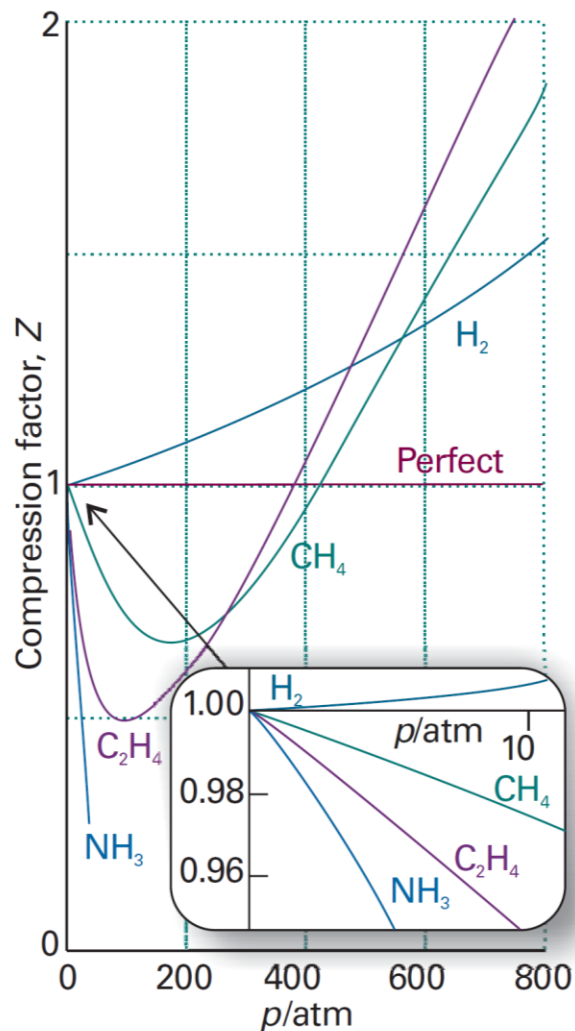


Fig. 1.14 The variation of the compression factor, Z , with pressure for several gases at 0°C . A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

Deviation from ideality: REAL GAS

Compression/compressibility factor:

$$Z(p, T) = V_m / V_m^\circ$$

$$Z(p, T) = pV_m / RT$$

- At very low pressure and high temp.; $Z \sim 1$ (Perfect gas behavior)
- At high p , molecular volume significant, repulsion dominates
 $V_m > V_{m,\text{ideal}} \rightarrow Z > 1$
- At intermediate p , (& low temp), insignificant molecular volume; attraction dominates
 $V_m < V_{m,\text{ideal}} \rightarrow Z < 1$

The Equation of State for Real Gases

Virial Equation of State

At very low pressure, real gases behave ideally. Hence, let the ideal gas law be the first term in a series in powers of a variable (p or $1/V_m$)

$$pV_m = RT(1 + B'p + C'p^2 \dots)$$

$$pV_m = RT(1 + B/V_m + C/V_m^2 \dots)$$

B' and C' are 2nd and 3rd virial coefficients (at temp T)

As, $p \rightarrow 0$, virial equation reproduces ideal gas equation.

$$Z = (1 + B'p + C'p^2) = (1 + B/V_m + C/V_m^2)$$

The properties of real gases *do not always* coincide with the perfect gas values at low pressures.

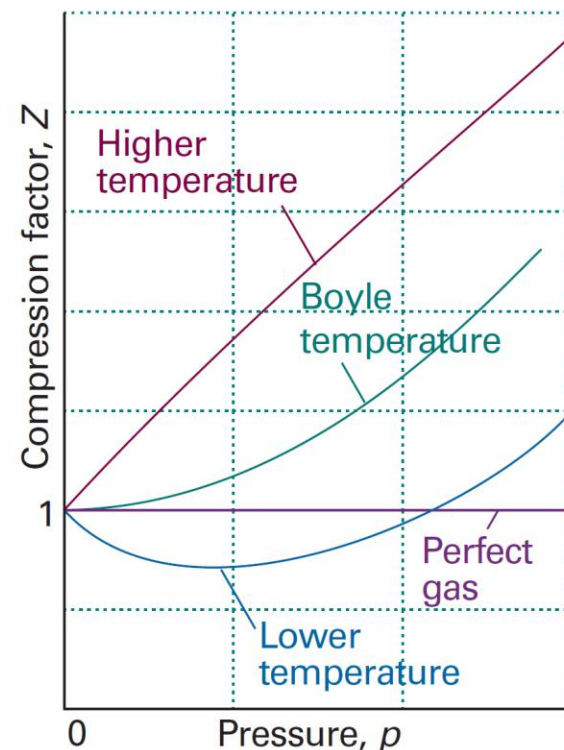
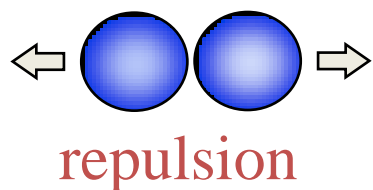


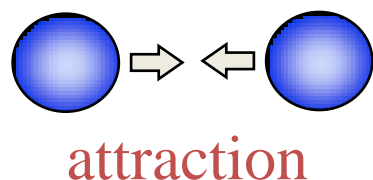
Fig. 1.16 The compression factor, Z , approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

The van der Waals model of real gases



$$V_{eff} = V - nb$$

$$p = \frac{nRT}{V} \quad (\text{Ideal gas equation})$$



$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

The van der Waals equation of state for real gases

- At high temperature and large volume, vdW equation reduces to ideal gas law.
- Liquid and gases coexist when attractive and repulsive forces balance
- Critical Constants and vdW parameters: $V_c = 3b$, $p_c = a/27b^2$, $T_c = 8a/27Rb$, $Z_c = p_c V_c / RT_c = 3/8$ (the critical compression factor)

$$\frac{dp}{dV_m} = 0 \text{ and } \frac{d^2 p}{dV_m^2} = 0$$

Chemical Potential of Pure Real Gas

$$\mu(T) = \mu^\circ(T) + RT \ln f$$

$$= \mu^\circ(T) + RT \ln \phi p$$

$$= \mu^{\text{ideal}}(T) + RT \ln \phi$$

f = fugacity, an effective pressure in bar = ϕp

ϕ = fugacity coefficient

$$\ln \phi = \int_0^p \frac{Z - 1}{p} dp \quad Z = \text{Compressibility factor}$$

At low pressure,

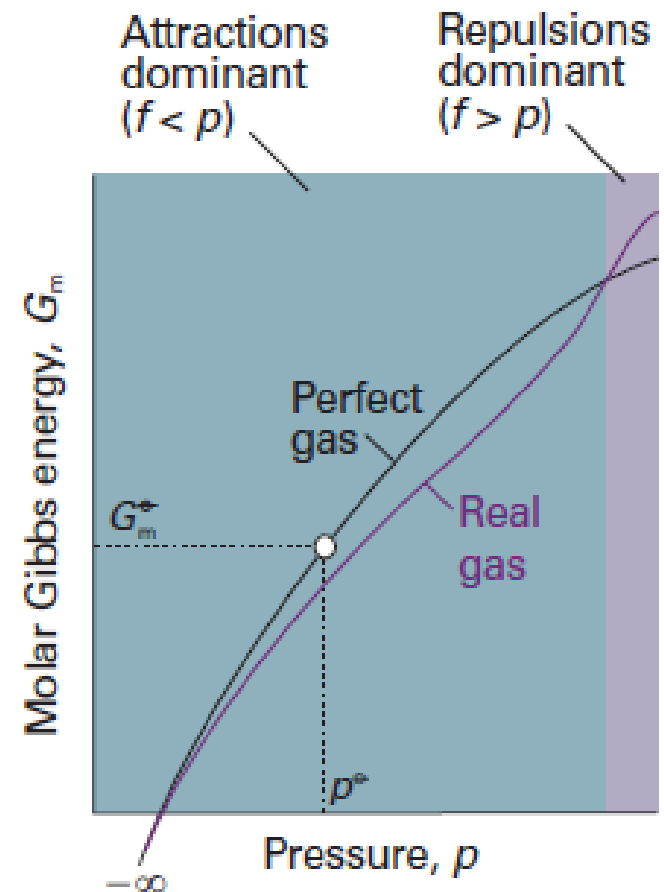
$$Z < 1 \Rightarrow \ln \phi < 0 \Rightarrow \mu^{\text{real}} < \mu^{\text{ideal}}$$

$$\phi < 1 \Rightarrow f < p$$

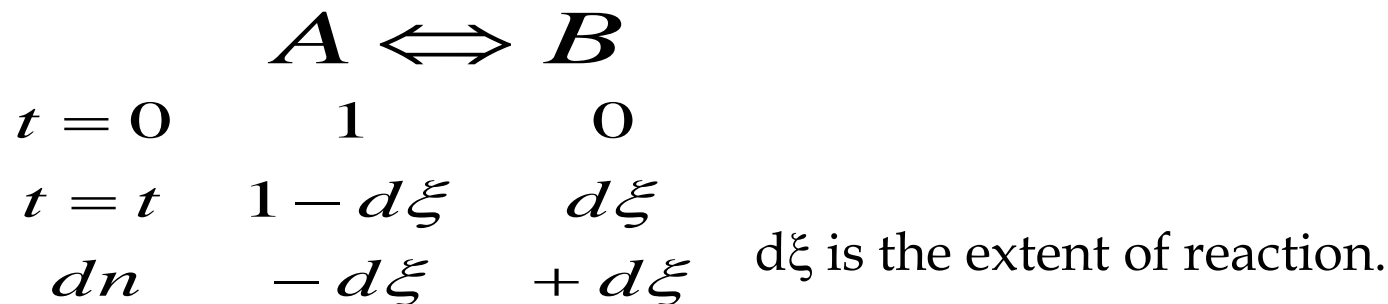
At high pressure,

$$Z > 1 \Rightarrow \ln \phi > 0 \Rightarrow \mu^{\text{real}} > \mu^{\text{ideal}}$$

$$\phi > 1 \Rightarrow f > p$$



Reaction Gibbs Energy ($\Delta_r G$)



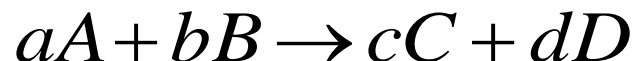
$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

$$\left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_B - \mu_A$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_B - \mu_A$$

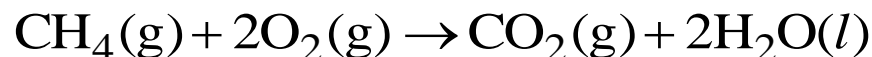
The reaction Gibbs energy is the difference between the chemical potential of product and reactant at the *composition of the reaction mixture*.

Reaction Gibbs Energy ($\Delta_r G$)



$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_i \nu_i \mu_i$$



$$\Delta_r G = (2\mu_{\text{H}_2\text{O}(\text{l})} + \mu_{\text{CO}_2(\text{g})}) - (\mu_{\text{CH}_4(\text{g})} + 2\mu_{\text{O}_2(\text{g})})$$

At equilibrium,

$$\sum_i \mu_i \nu_i = 0$$

Condition for chemical reaction equilibrium.

At the reaction equilibrium, the chemical potentials of the product balance those of the reactants

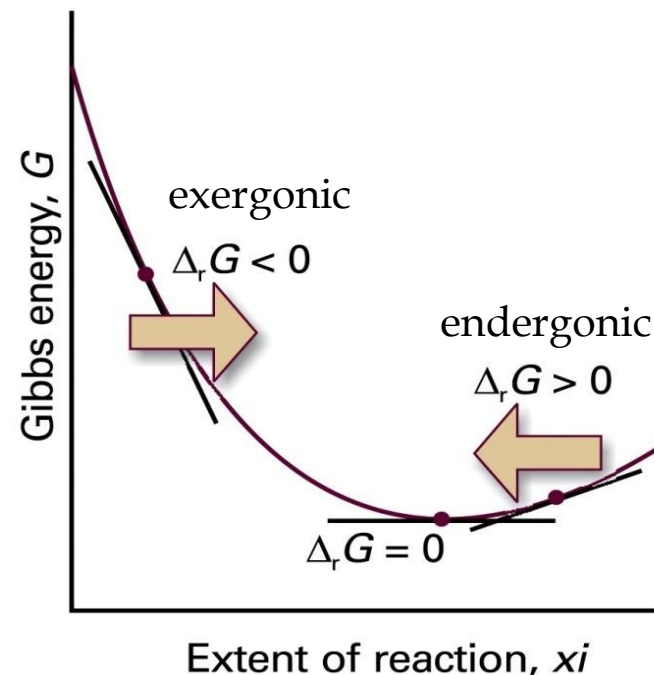


Figure 7-1
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Reaction Equilibrium

$$\begin{aligned}\Delta_r G &= \sum_i \nu_i \mu_i = \sum_i \nu_i [\mu_i^0(T) + RT \ln a_i] \\ &= \sum_i \nu_i \mu_i^0(T) + \sum_i RT \ln a_i^{\nu_i}\end{aligned}$$

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln \prod_i a_i^{\nu_i} = \Delta_r G^0(T) + RT \ln Q$$

$$Q = \prod_i a_i^{\nu_i}$$

The reaction Quotient
(at any extent of the reaction)

At equilibrium,

$$K = \left[\prod_i a_i^{\nu_i} \right]_{\text{at equilibrium}}$$

Thermodynamic
equilibrium constant

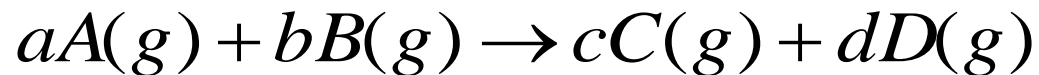
$$\Delta_r G^0 = -RT \ln K$$

$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K$$

Practically a_i approximated by numerical values of molalities /
by molar concentration / numerical values of partial pressures

Can be used to calculate
equilibrium constant for any
reaction from tables of
thermodynamic data.

Reaction Equilibrium in ideal gas reaction



$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln Q$$

$$Q = \prod_i a_i^{\nu_i} = \prod_i \left(\frac{p_i}{p^0} \right)^{\nu_i}$$

The reaction Quotient in terms of partial pressure (at any extent of reaction)
 $p^0 = 1 \text{ bar}$

At equilibrium,

$$K_p = \prod_i \left(\frac{p_i}{p^0} \right)^{\nu_i} \text{ (at equilibrium)}$$

$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K_p$$

$$\Delta_r G^0 = -RT \ln K_p$$

Different types of equilibrium constants

$$K = \left[\prod_i a_i^{\nu_i} \right]_{equilibrium}$$

Thermodynamic equilibrium constant in terms of activity coefficients (a_i)

$$K_p = \left[\prod_i p_i^{\nu_i} \right]_{equilibrium}$$

Standard equilibrium constant for gaseous reaction
 p_i (in bar units)

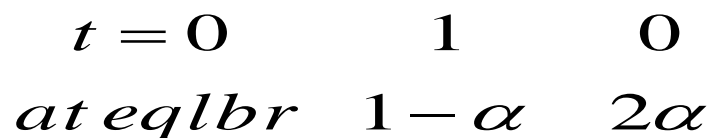
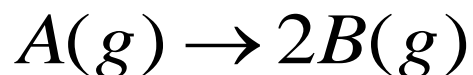
$$K_c = \left[\prod_i c_i^{\nu_i} \right]_{equilibrium}$$

Standard concentration equilibrium constant.
 c_i in mol/L

$$K_\chi = \left[\prod_i \chi_i^{\nu_i} \right]_{equilibrium}$$

Mole-fraction equilibrium constant

Response of equilibria to pressure change



$$\chi_i \quad \frac{1 - \alpha}{1 + \alpha} \quad \frac{2\alpha}{1 + \alpha}$$

$$p_i \quad \frac{1 - \alpha}{1 + \alpha} p \quad \frac{2\alpha}{1 + \alpha} p \quad p \text{ is in bar}$$

α is the degree of dissociation

$$K_p = \prod_i \left(\frac{p_i}{p^0} \right)^{\nu_i} = \frac{4\alpha^2}{1 - \alpha^2} p$$

But we know, $\left(\frac{\partial K_p}{\partial p} \right)_T = 0$

$$\alpha = \left(\frac{1}{1 + \frac{4p}{K_p}} \right)^{1/2}$$

Le-Chatelier principle

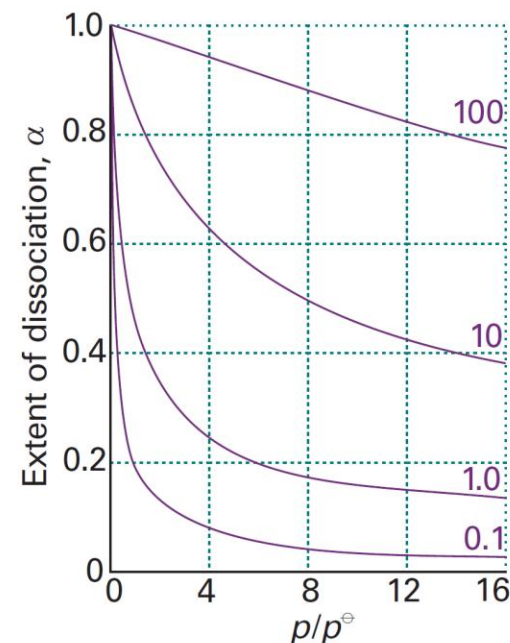


Fig. 7.7 The pressure dependence of the degree of dissociation, α , at equilibrium for an $A(g) \rightleftharpoons 2B(g)$ reaction for different values of the equilibrium constant K . The value $\alpha = 0$ corresponds to pure A; $\alpha = 1$ corresponds to pure B.

Temperature dependence of equilibrium constant

$$\Delta_r G^0 = -RT \ln K$$

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^0 / T)}{dT}$$

$$\frac{d(\Delta_r G^0 / T)}{dT} = -\frac{\Delta_r H^0}{T^2} \text{ (GibbsHelmholtzEquation)}$$

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2}} \quad \text{van't Hoff equation}$$

For exothermic reactions, K decreases with increasing T

$$\boxed{\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$