

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 12.2

Equilibrium Constants K_P , K_C , and K_a

$\Delta_r G$ AND STANDARD STATES

$$\Delta_r G = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B$$

At low enough partial pressures we expect ideal behavior (cf. video 9.7), $\mu_j(T, P) = \mu_j^\circ(T) + RT \ln\left(\frac{P_j}{P^\circ}\right)$

which permits definition of the **standard-state free energy of reaction:**

$$\Delta_r G^\circ(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$$

which is the change in G for unmixed reactants each at T and 1 bar forming unmixed products each at T and 1 bar.

What about the free energy change for *actual* partial pressures $P_j \neq P^\circ$?

$\Delta_r G$ AND STANDARD STATES (CONT.)

$$\Delta_r G = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B \quad \mu_j(T, P) = \mu_j^\circ(T) + RT \ln \left(\frac{P_j}{P^\circ} \right)$$

$$\Delta_r G(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T) \\ + RT \left[\nu_Y \ln \left(P_Y / P^\circ \right) + \nu_Z \ln \left(P_Z / P^\circ \right) - \nu_A \ln \left(P_A / P^\circ \right) - \nu_B \ln \left(P_B / P^\circ \right) \right]$$

Q is the reaction quotient $\ln Q = \ln \frac{\left(P_Y / P^\circ \right)^{\nu_Y} \left(P_Z / P^\circ \right)^{\nu_Z}}{\left(P_A / P^\circ \right)^{\nu_A} \left(P_B / P^\circ \right)^{\nu_B}}$

Note that $P^\circ = 1$ bar in this case and is therefore often not shown. However, you must remember that the standard-state pressure is in the denominator to have unitless arguments.

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

EQUILIBRIUM CONSTANT K_P

At *equilibrium* the Gibbs reaction energy is a minimum with respect to any displacement, i.e.,

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

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0 \quad (\text{equilibrium})$$

$$\Delta_r G^\circ(T) = -RT \ln Q_{\text{eq}} = -RT \ln \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

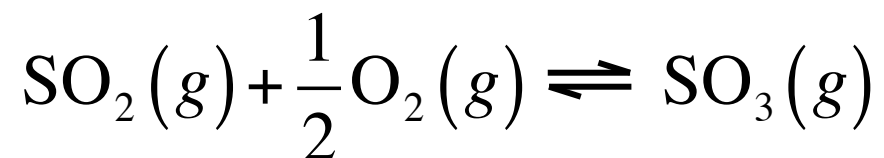
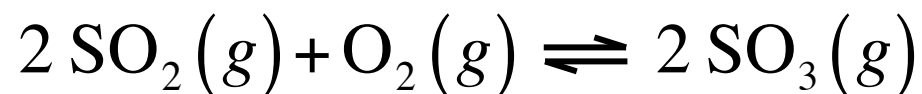
$$\Delta_r G^\circ(T) = -RT \ln K_P(T)$$

$$K_P(T) = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}}$$

The ***equilibrium constant***, which means the reaction quotient with all partial pressures *at their equilibrium values in standard-state units*.

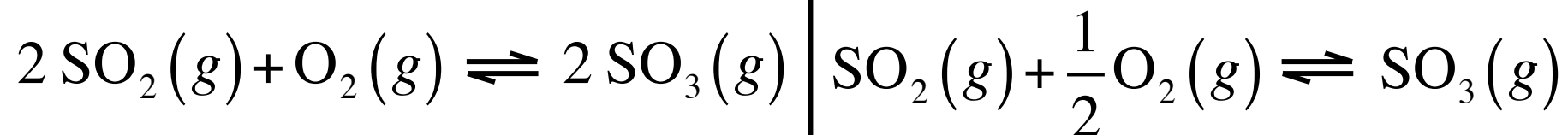
Self-assessment

Consider the reactions:



What is K_p for each, and how does K_p for the first compare to K_p for the second? Why is this comparison important?

Self-assessment Explained

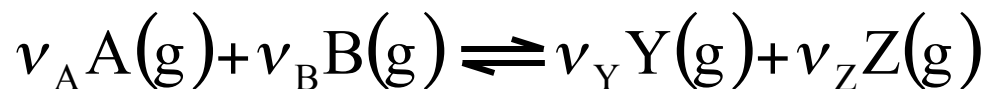


$$K_P(T) = \left(\frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} \right)_{\text{eq}}$$

$$K_P(T) = \left(\frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}} \right)_{\text{eq}}$$

Clearly, the equilibrium constant to the left is the square of the one to the right, even though the chemical reaction is the “same” other than the way in which the stoichiometry is written. Thus, equilibrium constants *must* be associated with a specific, balanced chemical reaction to be meaningfully interpreted!

EQUILIBRIUM CONSTANT K_c



Using the ideal gas relationship, $P = cRT$, we can convert the equilibrium constant to units of concentration,

$$K_P = \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{\text{eq}} \xrightarrow[\substack{P=cRT \\ c = \frac{n}{V}}]{\quad} K_P = \frac{c_Y^{\nu_Y} c_Z^{\nu_Z}}{c_A^{\nu_A} c_B^{\nu_B}} \left(\frac{RT}{P^\circ} \right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

Don't forget the reference state!

Multiply and divide each c by c° ,

$$K_P = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

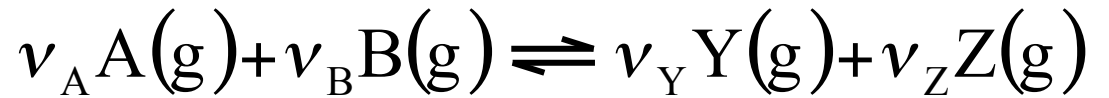
Unitless, so units of R depend on choice of units for c° and P°

$$K_c = \frac{\left(c_Y / c^\circ \right)^{\nu_Y} \left(c_Z / c^\circ \right)^{\nu_Z}}{\left(c_A / c^\circ \right)^{\nu_A} \left(c_B / c^\circ \right)^{\nu_B}}$$

(Often c° is taken as 1 M and not displayed, but don't forget that it's there!)

EQUILIBRIUM CONSTANT K_a

One can also express the equilibrium constant in terms of activities (for use in solution as opposed to with gases)



$$\Delta_r G = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B$$

$$\mu_j(T, P) = \mu_j^\circ(T) + RT \ln a_j$$

By analogy to K_c :

$$\Delta_r G = \Delta_r G^\circ(T) + RT \ln \left(\frac{a_Y^{\nu_Y} a_Z^{\nu_Z}}{a_A^{\nu_A} a_B^{\nu_B}} \right)$$

The *thermodynamic equilibrium constant*:

$$K_a(T) = \left(\frac{a_Y^{\nu_Y} a_Z^{\nu_Z}}{a_A^{\nu_A} a_B^{\nu_B}} \right)_{\text{eq}}$$

may be substantially less ideal with solutes in solution than mixtures of gases

$$\Delta_r G^\circ(T) = -RT \ln K_a(T)$$

$$dU = \delta q + \delta w$$



Next: Noxious Equilibrium Example