EG3029 Chemical Thermodynamics

Chemical Reaction Equilibrium

Reaction Coordinate
Single Reaction

- General chemical reaction:

$$|\nu_1|A_1 + |\nu_2|A_2 + \cdots \rightarrow |\nu_3|A_3 + |\nu_4|A_4 + \cdots$$

ν_i stoichiometric coefficient
A_i chemical species

- Change in quantities as reaction progresses:

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = \cdots$$

- Reaction coordinate ε

$$\frac{dn_i}{\nu_i} = d\varepsilon$$

$$dn_i = \nu_i d\varepsilon$$

- Mole fractions of species

$$y_i = \frac{n_i}{n} = \frac{n_{i,0} + \nu_i \varepsilon}{n_0 + \nu \varepsilon}$$

Reaction Coordinate Multireaction

- Multireaction progress:

$$\boxed{dn_i = \sum_j \nu_{i,j} d\varepsilon_j}$$

- Mole fractions of species:

$$\boxed{y_i = \frac{n_{i,0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j \varepsilon_j}}$$

j **reaction index**

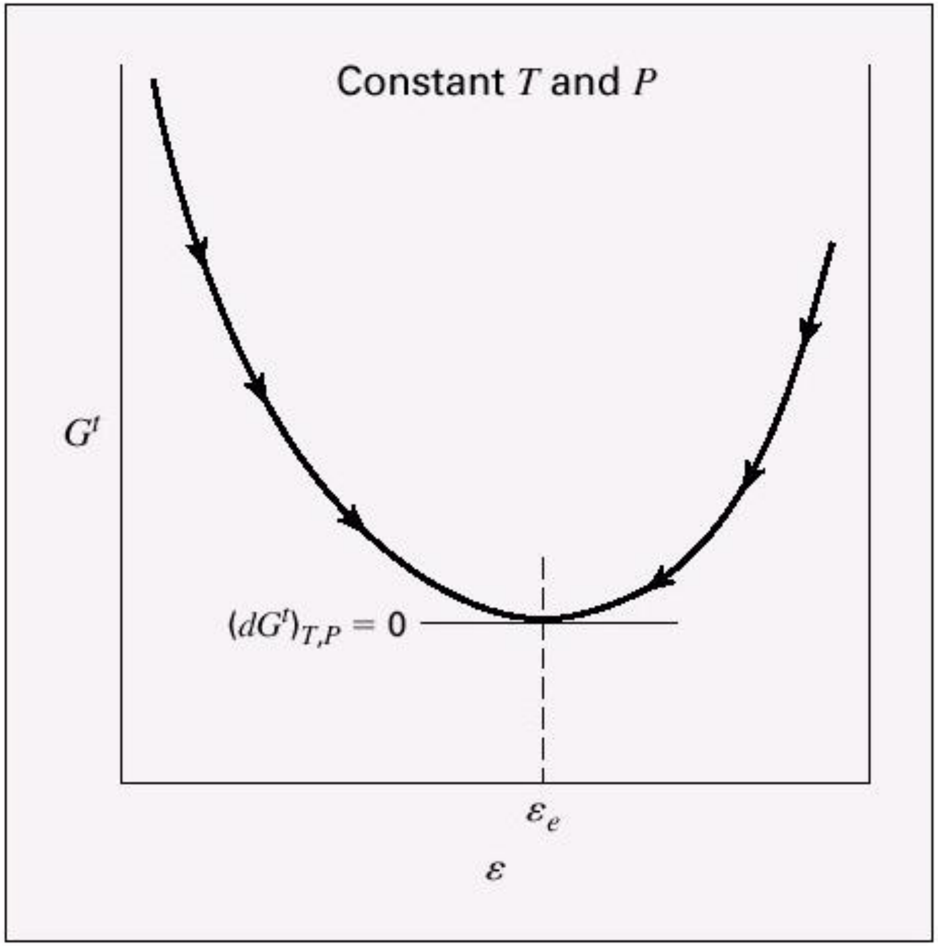
Reaktion					A[cm,mol,s]	b	E/kJ·mol^{-1}
----	01. - 04. H_2-CO Oxidation						
----	01. H_2-O_2-Reaktionen (HO_2, H_2O_2 ausgeschlossen)						
O_2	+H		=OH	+O	$2.00\cdot10^{14}$	0.0	70.3
H_2	+O		=OH	+H	$5.06\cdot10^{04}$	2.67	26.3
H_2	+OH		=H_2O	+H	$1.00\cdot10^{08}$	1.6	13.8
OH	+OH		=H_2O	+O	$1.50\cdot10^{09}$	1.14	0.42
H	+H	+M*	=H_2	+M*	$1.80\cdot10^{18}$	-1.0	0.00
O	+O	+M*	=O_2	+M*	$2.90\cdot10^{17}$	-1.0	0.00
H	+OH	+M*	=H_2O	+M*	$2.20\cdot10^{22}$	-2.0	0.00
----	02. HO_2-Bildung/Verbrauch						
H	+O_2	+M*	=HO_2	+M*	$2.30\cdot10^{18}$	-0.8	0.00
HO_2	+H		=OH	+OH	$1.50\cdot10^{14}$	0.0	4.20
HO_2	+H		=H_2	+O_2	$2.50\cdot10^{13}$	0.0	2.90
HO_2	+H		=H_2O	+O	$3.00\cdot10^{13}$	0.0	7.20
HO_2	+O		=OH	+O_2	$1.80\cdot10^{13}$	0.0	-1.70
HO_2	+OH		=H_2O	+O_2	$6.00\cdot10^{13}$	0.0	0.00
----	03. H_2O_2-Bildung/Verbrauch						
HO_2	+HO_2		=H_2O_2	+O_2	$2.50\cdot10^{11}$	0.0	-5.20
OH	+OH	+M*	=H_2O_2	+M*	$3.25\cdot10^{22}$	-2.0	0.00
H_2O_2	+H		=H_2	+HO_2	$1.70\cdot10^{12}$	0.0	15.7
H_2O_2	+H		=H_2O	+OH	$1.00\cdot10^{13}$	0.0	15.0
H_2O_2	+O		=OH	+HO_2	$2.80\cdot10^{13}$	0.0	26.8
H_2O_2	+OH		=H_2O	+HO_2	$5.40\cdot10^{12}$	0.0	4.20
----	04. CO-Reaktionen						
CO	+OH		=CO_2	+H	$6.00\cdot10^{06}$	1.5	-3.10
CO	+HO_2		=CO_2	+OH	$1.50\cdot10^{14}$	0.0	98.7
CO	+O	+M*	=CO_2	+M*	$7.10\cdot10^{13}$	0.0	-19.0
CO	+O_2		=CO_2	+O	$2.50\cdot10^{12}$	0.0	200.

Elementary reactions in methane/air combustion. from Warnatz, Maas, Dibble, 'Combustion' (97)

Reaction Equilibrium
General

- In a closed system at constant T and P, the reaction equilibrium is reached when the total Gibbs energy attains its minimum value:

$$\left(dG^t\right)_{T,P} = 0$$



Reaction Equilibrium
Equilibrium Constant

- Criterion: $$\sum_i \nu_i \mu_i = 0$$

- Equilibrium constant *K*:

$$\prod_i \left(\frac{\hat{f}_i}{f_i^\circ} \right)^{\nu_i} = K = \exp\left(\frac{-\Delta G^\circ}{RT} \right)$$

- Standard heat of reaction:

$$\Delta H^\circ = -RT^2 \frac{d\left(\Delta G^\circ / RT\right)}{dT}$$

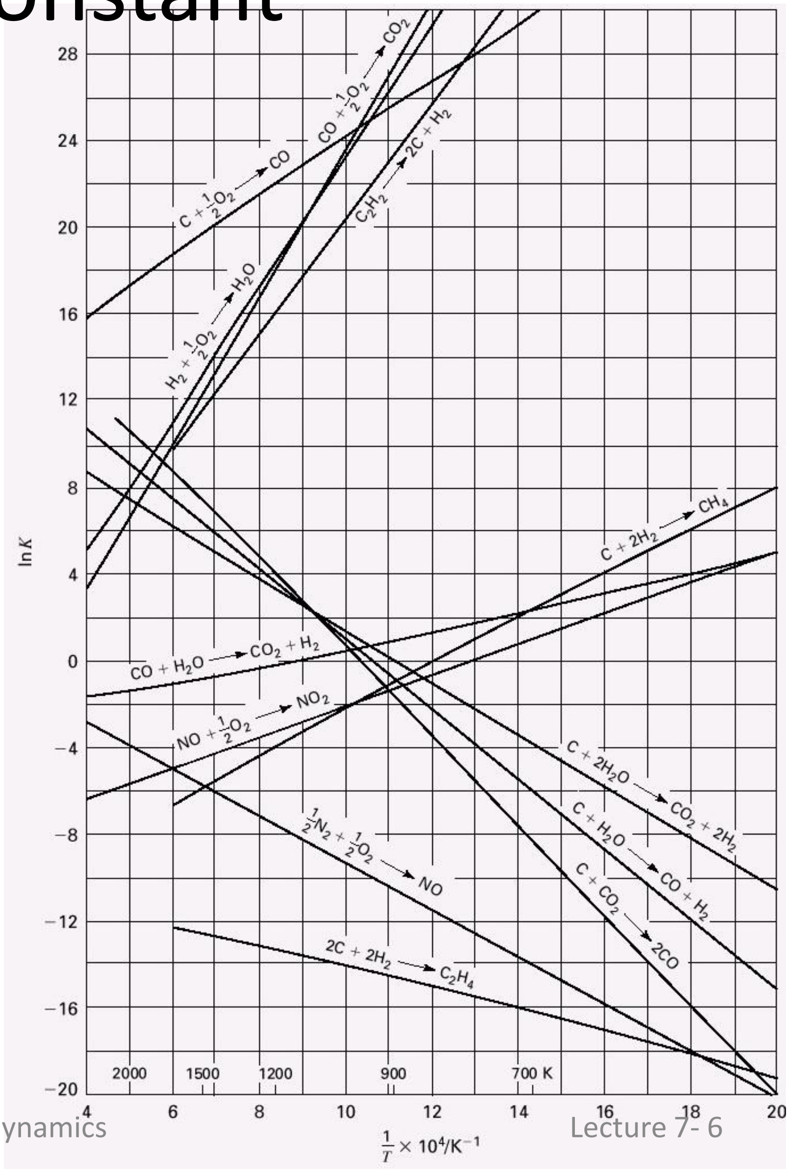
Reaction Equilibrium
Equilibrium Constant

- Temperature effects...
  - on equilibrium constant

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

  - on standard heat of reaction

$$\Delta H^\circ = \Delta H_0^\circ + R\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\, dT$$



Reaction Equilibrium
Equilibrium Constant

- Composition effects...
  - in gas-phase reactions

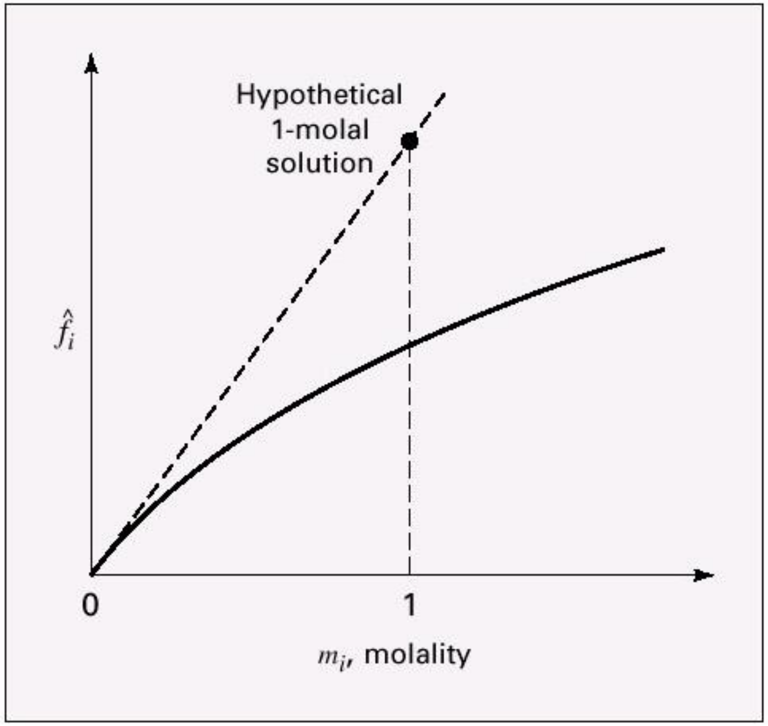
$$\boxed{\prod_i \left(y_i \phi_i\right)^{\nu_i} = K \cdot \left(\frac{P}{P^\circ}\right)^{-\nu}}$$

  - in liquid-phase reactions

$$\boxed{\prod_i \left(y_i \gamma_i\right)^{\nu_i} = K \cdot \exp\left(\frac{\left(P^\circ - P\right)}{RT} \sum_i \left(\nu_i V_i\right)\right)^{-\nu}}$$

  - Equilibrium conversion ε_e

Standard state for dilute aqueous solutions.



Phase Rule

- For a non-reacting multi-phase multi-component system:

$$\boxed{F = 2 - \pi + N}$$

F degrees of freedom
π number of phases
N number of chem. species

- For a multi-phase multi-component system in which r chemical reactions take place:

$$\boxed{F = 2 - \pi + N - r}$$

Multi-reaction Equilibrium

- For a gas-phase system (ideal gas):

$$\prod_i (y_i)^{\nu_{i,j}} = \left(\frac{P}{P^\circ}\right)^{-\nu_j} \cdot K_j$$

- Elemental material balance

$$\sum_i n_i a_{ik} = A_k$$

k element
i molecular species
A total number of atomic masses
a number of atoms

- Standard Gibbs energy change:

$$\Delta G^\circ_{f_i} + RT \ln\left(\frac{y_i \hat{\phi}_i P}{P^\circ}\right) + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1,2,\ldots,N)$$

Multi-reaction Equilibrium

Worked example: A bed of coal (carbon) in a coal gasifier is fed with steam and air, and produces a gas stream containing H_2, CO, O_2, H_2O, CO_2, and N_2. If the feed to the gasifier consists of 1 mol of steam and 2.38 mol of air, calculate the equilibrium composition of the gas stream at P = 20 bar for temperatures of 1000 and 1500 K.

	ΔG°_{f} / J mol^{-1}		
T / K	H_2O	CO	CO_2
1000	-192,420	-200,240	-395,790
1500	-164,310	-243,740	-396,160