



Aalto University

CHEM-E6100

Fundamentals of chemical thermodynamics

Week 4, Fall 2022

Contents

- **Summary about state functions**
 - **Size of a system (Ch 5.6)**
 - **Fundamental equation of thermodynamics**
 - **Chemical potential (Ch 5.7)**
 - **Concept of activity**
 - **General criterion of equilibrium**
 - **Maxwell's relation (Ch 5.9)**
 - **Impact of pressure on properties of substances**
-

Intended learning outcomes for Week 4

After the lectures of Week 4, it is expected that the student:

- **can derive the differential forms of the thermodynamic functions H , A , and G**
- **understands the term ‘chemical potential’ and how it is derived**
- **understands the relation between activity, equilibrium constants and gibbs energy of a reaction**
- **knows how to interpret the Maxwell relations**

Summary of the state functions

- It was shown earlier that the change of internal energy (U) can be expressed as:
$$dU = TdS - PdV$$
- With our focus on the chemical equilibria, we get the relations between the key variables from their definitions as:

- $H = U + PV$ or in differential form $dH = TdS + VdP$
- $A = U - TS$ or in differential form $dA = -SdT - PdV$
- $G = H - TS$ or in differential form $dG = -SdT + VdP$
- $d(TS) = TdS + SdT$
- $d(PV) = PdV + VdP$

Differentiation Rules	
Constant Rule	$\frac{d}{dx}[c] = 0$
Power Rule	$\frac{d}{dx}x^n = nx^{n-1}$
Product Rule	$\frac{d}{dx}[f(x)g(x)] = f'(x)g(x) + f(x)g'(x)$
Quotient Rule	$\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right] = \frac{g(x)f'(x) - f(x)g'(x)}{[g(x)]^2}$
Chain Rule	$\frac{d}{dx}[f(g(x))] = f'(g(x))g'(x)$

Summary of the state functions

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- $d(TS) = TdS + SdT$
- $d(PV) = PdV + VdP$

$$dH = ?$$

$$dA = ?$$

$$dG = ?$$

Size of a system

- The previous study concerned 'rational' state variables and their relations with the (practical) state variables
- How do the state functions behave when the size of the system (also its amount(s)) vary?
- The general mathematical expression for a function of three variables (in general amounts +2) gives us:
 - An infinitesimal change of any function $F = F(P, T, n_k)$ can be expressed by the (differential) changes of its variables T , P and n_k as
$$dF = (\partial F / \partial T)_{P, n_k} dT + (\partial F / \partial P)_{T, n_k} dP + \sum_k (\partial F / \partial n_k)_{P, T, n_j} dn_k, k \neq j$$

Size of a system

- The infinitesimal change of any function $F = F(P, T, n_k)$

$$dF = (\partial F / \partial T)_{P, n_k} dT + (\partial F / \partial P)_{T, n_k} dP + \sum_k (\partial F / \partial n_k)_{P, T, n_j} dn_k, k \neq j$$

is called total differential of function F

- It is obtained as a sum of the tangents of function F in respect of every variable, when the other variables are constant, multiplied by its difference
- For example tangent = $(\partial F / \partial T)$, difference = dT
- The sum is calculated over all components of the system

Chemical potential

- Change of Gibbs energy is governed (*in closed systems*) by the differential equation

$$dG = -SdT + VdP$$

- When we write accordingly the change of Gibbs energy as a function of temperature and pressure as well as the amounts (of components), we get

$$dG = (\partial G/\partial T)_{P,n_k}dT + (\partial G/\partial P)_{T,n_k}dP + \sum_k (\partial G/\partial n_k)_{P,T,n_j}dn_k, k \neq j$$

$$(\partial G/\partial T)_{P,n_k} = -S \text{ and } (\partial G/\partial P)_{T,n_k} = V$$

- The third term is the key variable in chemical equilibria, the chemical potential of component k (μ) and it is simply partial differential of Gibbs energy and amount $\mu = (\partial G/\partial n_k)_{P,T,n_j}$

Chemical potential

- Correspondingly as we get for Gibbs energy

$$dG = -SdT + VdP + \sum_k \mu_k dn_k$$

- Internal energy, enthalpy and Helmholtz energy are of the form

- $dU = TdS - PdV + \sum_k (\partial U / \partial n_k)_{S,V,n_j} dn_k$

- $dH = TdS - VdP + \sum_k (\partial H / \partial n_k)_{S,P,n_j} dn_k$

- $dA = -SdT + PdV + \sum_k (\partial A / \partial n_k)_{T,V,n_j} dn_k$

Chemical potential

- Because the change of components amounts always reflects in the system as an equally large change in its state of energy we can conclude that
- $(\partial G / \partial n_k)_{T,P,n_j} = \mu_k$
- $\mu_k = (\partial U / \partial n_k)_{S,V,n_j} = (\partial H / \partial n_k)_{S,P,n_j} = (\partial A / \partial n_k)_{T,V,n_j}$
- The chemical potential describes the change of substance's state of energy when its amount varies

The fundamental equation of thermodynamics

- ▶ By combining the 1st law and 2nd law for an open system in internal equilibrium and in equilibrium with the surroundings, gives the *fundamental equation of thermodynamics*

$$dU = TdS - PdV + \sum \mu_i dn_i$$

- ▶ μ_i is the chemical potential of particle /
- ▶ Including non-expansion work, such as in a galvanic cell gives:

$$dU = TdS - PdV + \sum \mu_i dn_i + dW_{rev(non-PV)}$$

Gibbs energy, G

- ▶ Rearranging the fundamental equation gives the definition of Gibbs energy

$$U - TS + PV = \sum \mu_i n_i$$

$$G = U - TS + PV$$

$$G = \sum \mu_i n_i$$

- ▶ The Gibbs energy function compresses all main state functions and variables of thermodynamics into one expression

$$H = U + PV \rightarrow G = H - TS$$

- ▶ A similar function called Helmholtz energy can also be defined

$$A = U - TS$$

Chemical potential

The chemical potential, μ_i , of species i is related to Gibbs energy by

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

Chemical potential is the same as the partial molar Gibbs energy at constant P , T , and n_j

For a pure substance

$$\mu_i^* = \frac{G^*}{n_i} = G_m^*$$

Activity

- ▶ Activity is closely related to chemical potential
- ▶ Chemical potentials are the driving force for distribution of components between phases of variable compositions
- ▶ Activity can be thought of as the parameter that gives the effective “availability” of component i for reaction in the system

Activity

- ▶ The relation between chemical potential and activity is given by

$$\mu_i = \mu_i^o + RT \ln a_i$$

Chemical potential of i in a phase

Standard state chemical potential of i in a phase

Activity of i in a phase

Phase in question may be given by the superscript

- ▶ The activity is a measure of the difference in the chemical potential between the studied state and the reference state
- ▶ Choice of reference state is therefore necessary and critical for activity determination

Activity

- ▶ For practical purposes various standard states are used for different types of phases

Ideal gas: $a_i = \frac{p_i}{p_i^o}$  1 bar of pure ideal gas i at T

Aqueous solutions: $a_i = \frac{c_i}{c_i^o}$

Activity coefficient, $\gamma=1$ for ideal solutions 

Solutions in general: $a_i = \gamma_i x_i$

General criterion of equilibrium

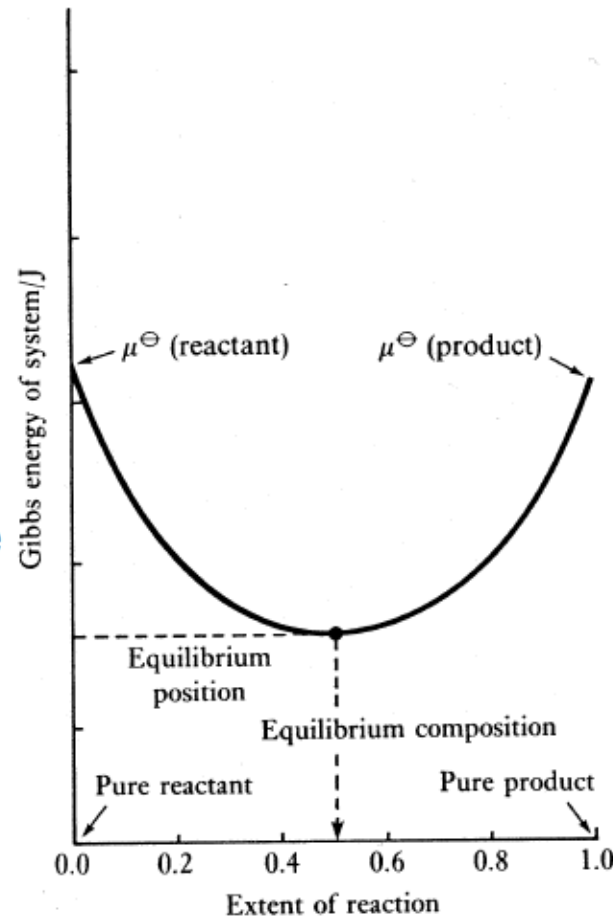
- The general criterion of equilibrium gives the *necessary and sufficient* conditions - from thermodynamic point of view - for the state of equilibrium.
- It expresses what features the properties of a system must in minimum fulfil when it is in equilibrium or the properties of the equilibrium point.
- In thermodynamic equilibrium the system is in:
 1. **thermal equilibrium** or all its phases ($\alpha, \beta, \dots$) have the same temperature: ${}^{\alpha}T = {}^{\beta}T = \dots = T$.
 2. **mechanical equilibrium** or all its phases have the same pressure: ${}^{\alpha}P = {}^{\beta}P = \dots = P$.
 3. **chemical equilibrium** or each component $i=1-N$ has the same chemical potential (partial molar Gibbs energy) in all phases of the system:
$${}^{\alpha}\mu_1 = {}^{\beta}\mu_1 = \dots = \mu_1 ; \quad {}^{\alpha}\mu_2 = {}^{\beta}\mu_2 = \dots = \mu_2 ; \dots ; \quad {}^{\alpha}\mu_N = {}^{\beta}\mu_N = \dots = \mu_N.$$
- When conditions 1-3 are simultaneously fulfilled the system is in the state of equilibrium.
- There could be other conditions (e.g. **electrical** equilibrium, if system has also charged species)

General criterion of equilibrium

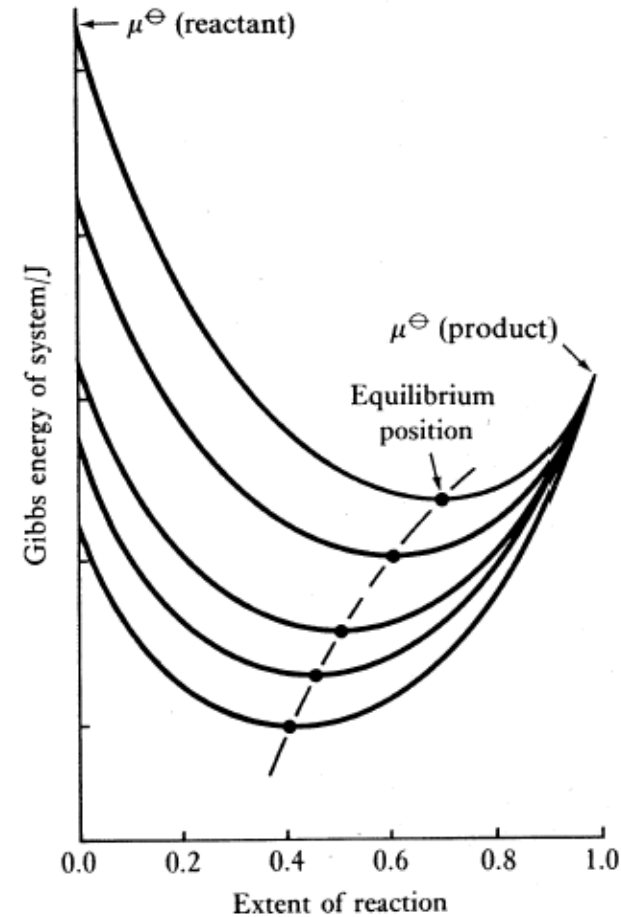
- The above criterion follows that the state of equilibrium is characterised by the minimum value of the system Gibbs energy, expressed also as

$$G_{eq} = (\sum \nu_i \cdot G_i)_{T,P,min}$$

- Also Helmholtz function has the minimum value in isothermal and isochoric process.



(a) $\mu^\ominus$ (reactant) = $\mu^\ominus$ (product)



(b) $\mu^\ominus$ (reactant) $\neq$ $\mu^\ominus$ (product)

- As stated in the definition of entropy, the system entropy in the point of equilibrium reaches its maximum value: $S_{eq} = (\sum \nu_i \cdot S_i)_{T,P,max}$.

Gibbs energy and the equilibrium constant

(Ch. 11.2)

- Law of mass action
- $jA + kB \rightleftharpoons lC + mD$
- K = equilibrium constant, a = activity
- Example: $1\text{CO} + 1\text{H}_2\text{O} \rightleftharpoons 1\text{CO}_2 + 1\text{H}_2$

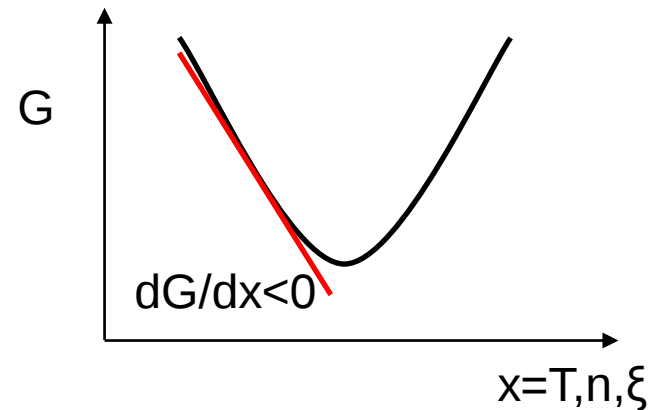
$$K = \frac{a_C^l a_D^m}{a_A^j a_B^k}$$

$$K = \frac{a_{\text{CO}_2}^1 a_{\text{H}_2}^1}{a_{\text{CO}}^1 a_{\text{H}_2\text{O}}^1}$$

- $\Delta G^\circ_{\text{rxn}} = -RT \ln K$ or $K = e^{-\Delta G^\circ / RT}$

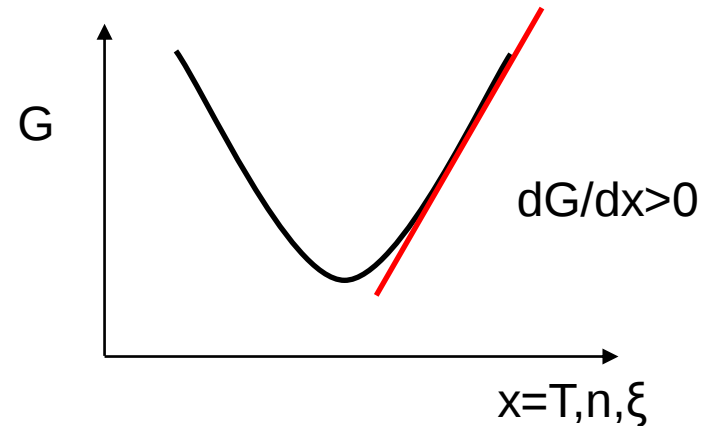
Gibbs energy and equilibrium constant

- Reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
- $K = [a(\text{CO}_2) \cdot a(\text{H}_2)] / [a(\text{CO}) \cdot a(\text{H}_2\text{O})]$
- $K = e^{-\Delta G/RT}$; ΔG is the change in Gibbs energy for the reaction ($G_{\text{CO}_2} + G_{\text{H}_2} - G_{\text{CO}} - G_{\text{H}_2\text{O}}$)
- $\Delta G < 0$: reaction favors $\text{CO}_2 + \text{H}_2$



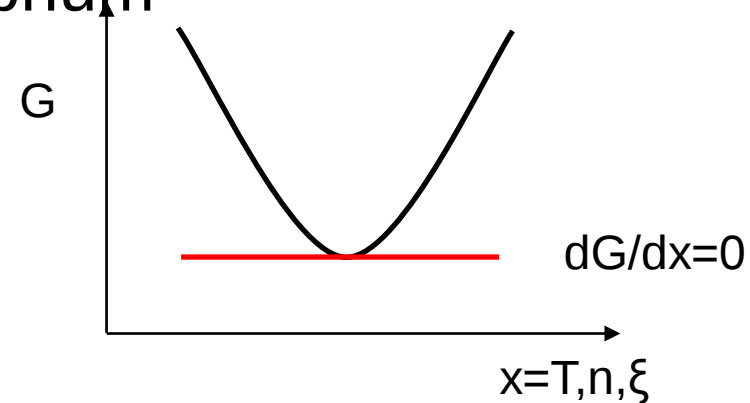
Thermodynamic concepts

- Reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
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Thermodynamic concepts

- Reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
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- $\Delta G < 0$: reaction favors $\text{CO}_2 + \text{H}_2$
- $\Delta G > 0$: reaction favors $\text{CO} + \text{H}_2\text{O}$
- $\Delta G = 0$: chemical equilibrium

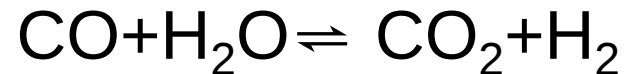


Conditions for Chemical Equilibrium

Minimum of Total Gibbs Energy

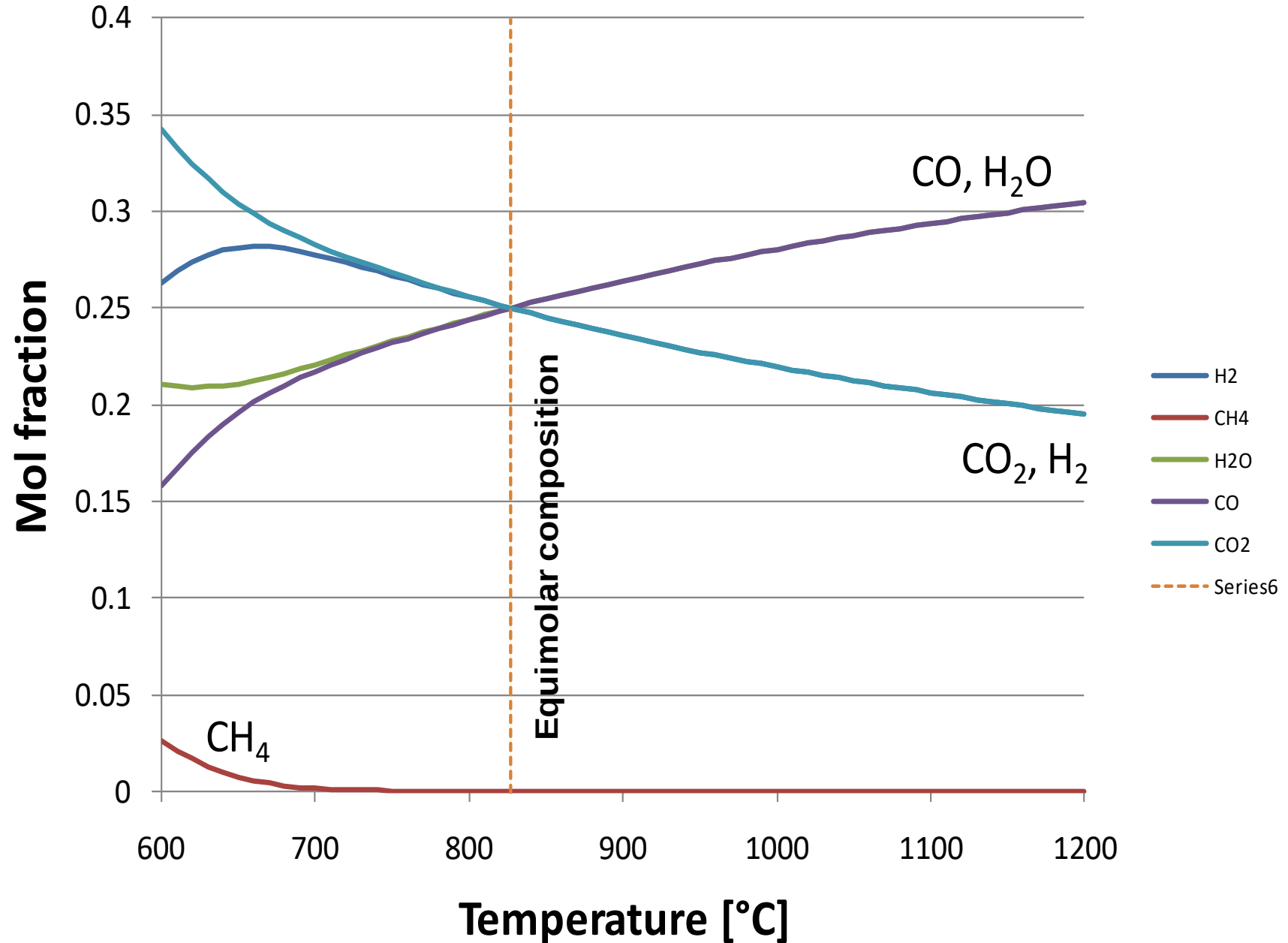
Water-gas shift reaction

- Syngas (synthesis gas), a mixture of CO + H₂, can be used to produce electricity or for diesel production in the Fischer-Tropsch processes
- Syngas is produced by steam reforming of CH₄/natural gas or gasification of woody biomass
- Syngas (CO+H₂) will react with CO₂ or H₂O

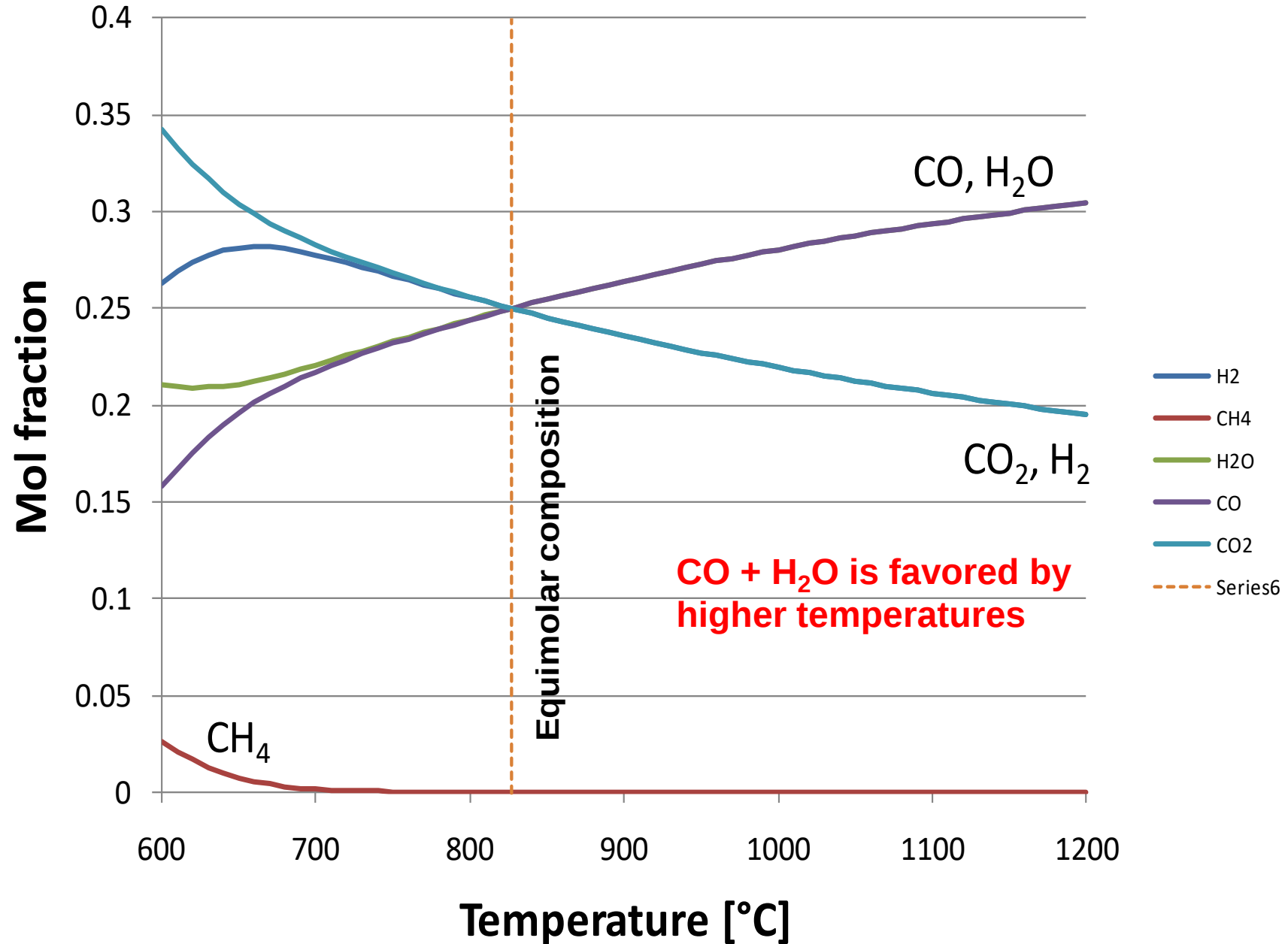


- Reaction is used to control/change CO/H₂ ratio in syngas
- Affects the gas composition in gasification processes

Water-gas shift reaction (1 bar)



Water-gas shift reaction (1 bar)



Consider the water gas shift reaction



Note:

- three elements (components): C, H, O
- one phase: gas
- no change in number of molecules during reaction

When is this single reaction valid?

At some overall composition O_2 , CH_4 and C-s may start to form.

The total composition is determined **entirely** by the amounts of the three **system components**.

At any state:

$$C_{\text{tot}} = n\text{CO} + n\text{CO}_2$$

$$H_{\text{tot}} = 2n\text{H}_2 + 2n\text{H}_2\text{O}$$

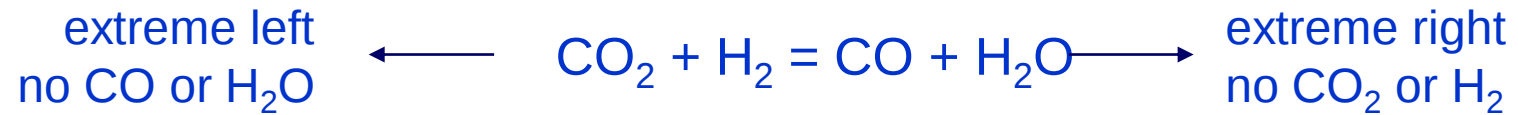
$$O_{\text{tot}} = n\text{CO} + n\text{H}_2\text{O} + 2n\text{CO}_2$$

The amount of the three components can **all** vary freely in the range

$$1 < O_{\text{tot}} / C_{\text{tot}} < 2 + 0.5 H_{\text{tot}}$$

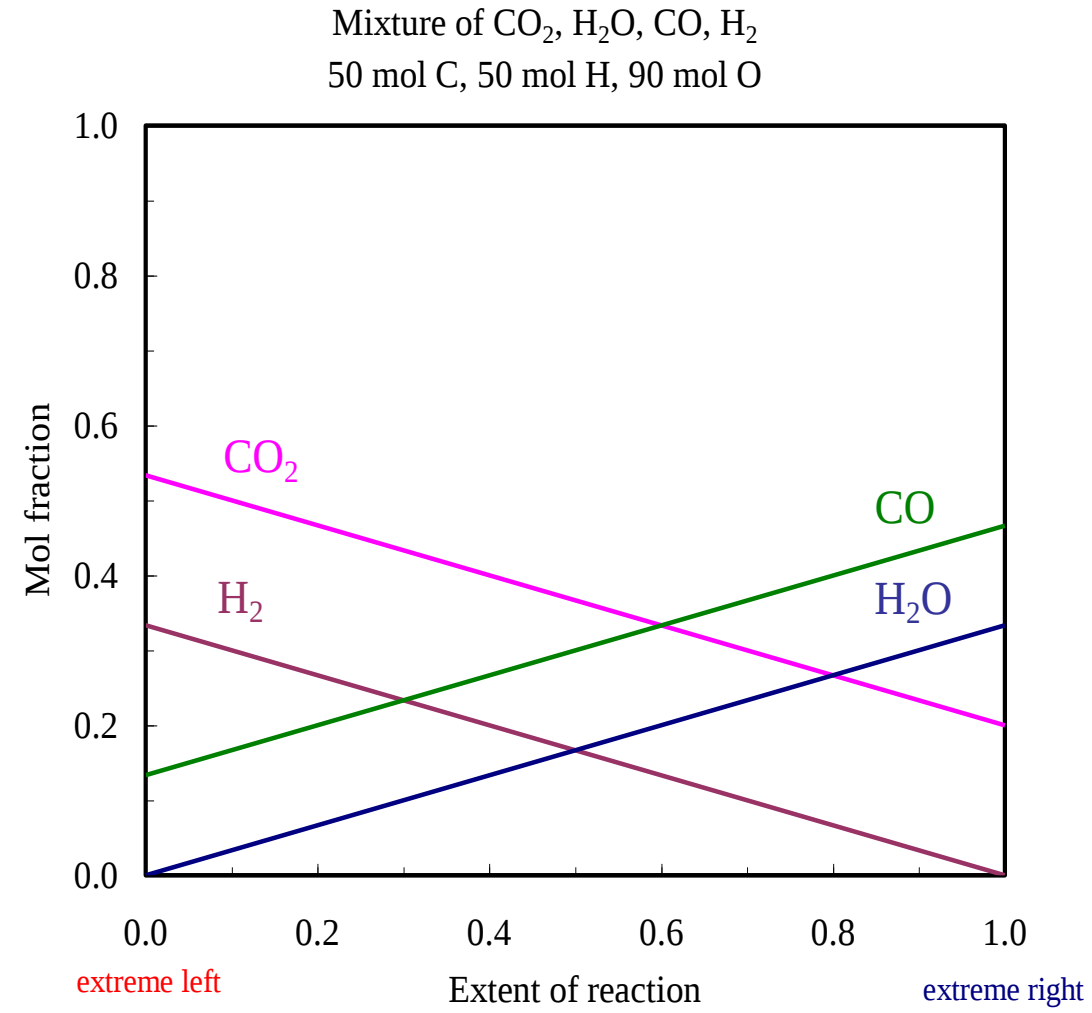
At given total amounts of the components there always will be a mixture of the four species CO_2 , H_2 , CO and H_2O .

Two extreme positions of the reaction can be recognized.



the equilibrium state is located somewhere between these extremes

The concept of extent of reaction can be used to determine the position



The "start situation" does not have to be one of extremes.

In technical application it can be any state satisfying the mass balance.

The "start situation" does not affect the equilibrium state, it is not necessary to define it, unless simultaneous energy balance calculations are needed.

Definitions like "before" and "after" are sometimes misleadingly used in equilibrium calculations to determine the mass balance restrictions.

The system is in chemical equilibrium when its Gibbs Energy is at the lowest possible value.

We search for the combination of amounts of CO₂, CO, H₂O and H₂ with the special feature that a small change in mol fraction for any of species leads to a higher total Gibbs Energy for the system.

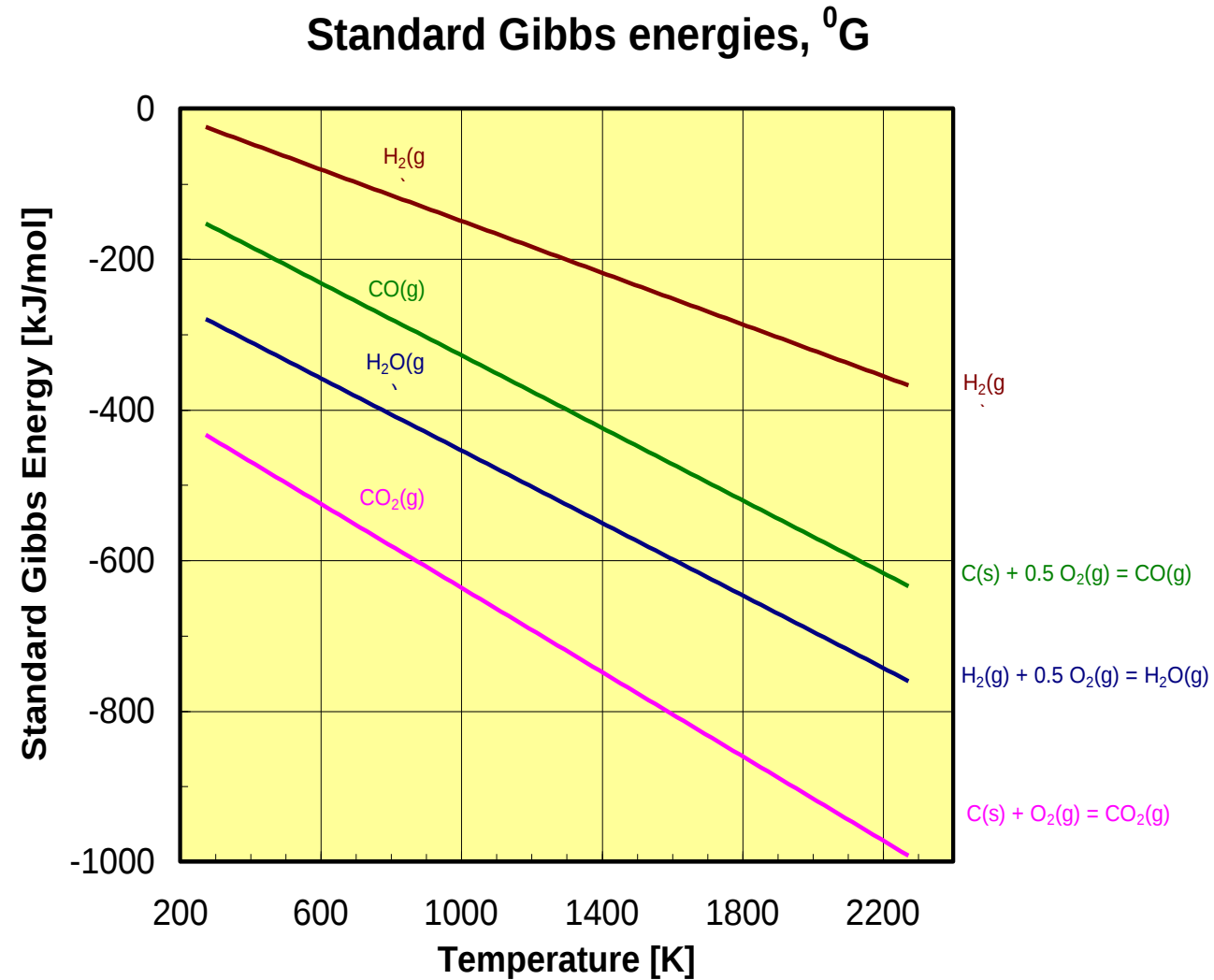
The total Gibbs Energy [J/mol] at constant temperature T is

$${}^T G_{\text{tot}} = x_{\text{CO}_2} {}^0 G_{\text{CO}_2} + x_{\text{CO}} {}^0 G_{\text{CO}} + x_{\text{H}_2\text{O}} {}^0 G_{\text{H}_2\text{O}} + x_{\text{H}_2} {}^0 G_{\text{H}_2} + \text{standard values}$$

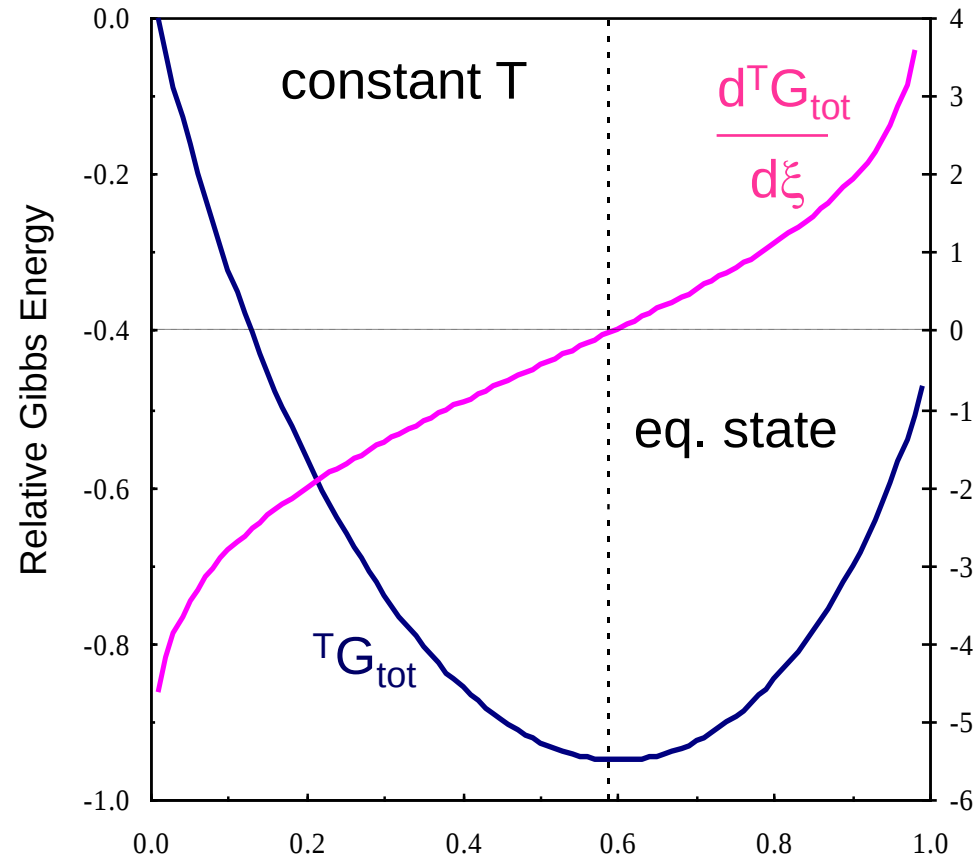
$$RT(x_{\text{CO}_2} \ln x_{\text{CO}_2} + x_{\text{CO}} \ln x_{\text{CO}} + x_{\text{H}_2\text{O}} \ln x_{\text{H}_2\text{O}} + x_{\text{H}_2} \ln x_{\text{H}_2}) + G^E$$

ideal mixing term excess Gibbs Energy

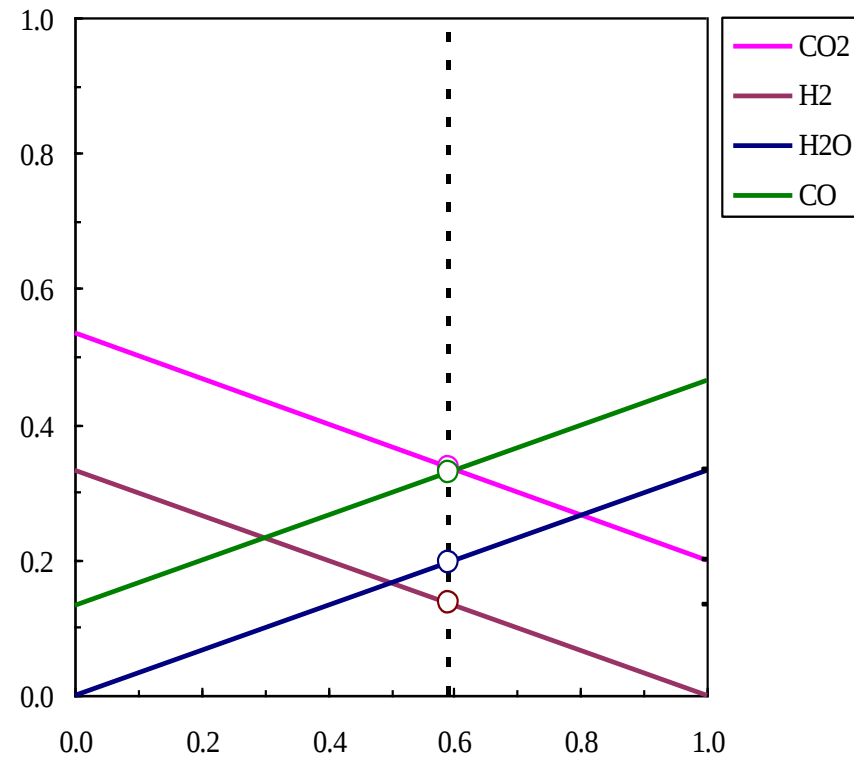
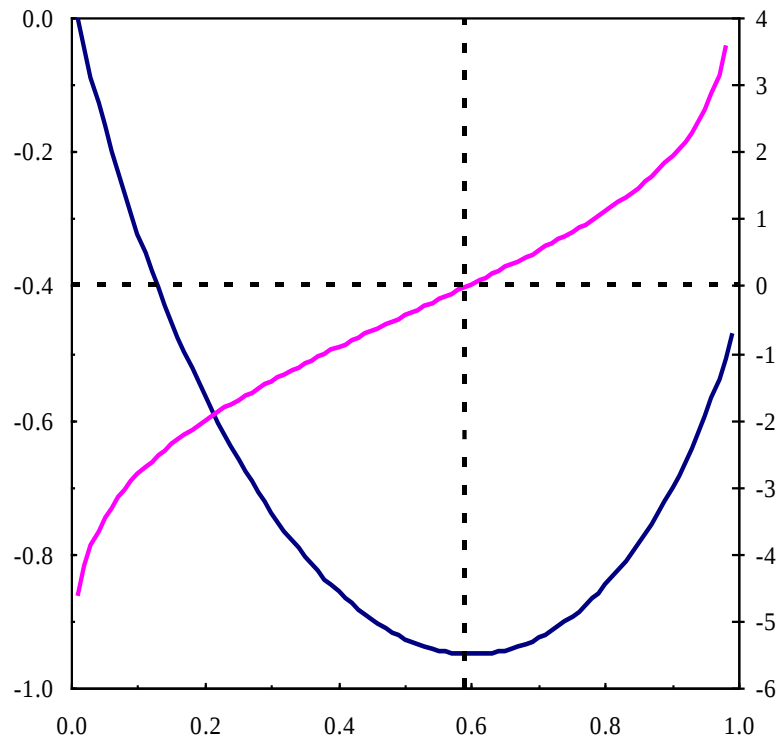
Standard Gibbs Energies are tabulated and relate to conventions of reference state



The total Gibbs Energy can be expressed as a function of extent of reaction and can be numerically calculated and derived in the whole range



The eq. composition is simultaneously determined



Conclusions

Equilibrium state can be determined if we **know**

- all possible species and phases
- standard Gibbs energy for all species
- total amount of all system components
- non-ideality (excess Gibbs Energy function)

We do **not** need to use or know

- reaction equations
- equilibrium constants
- state "before" equilibrium is established

Maxwell relations

The previous relations, after comparing the state functions and their state variables, yield for the common properties of the system

- temperature $T = (\partial U / \partial S)_{V,nk} = (\partial H / \partial S)_{P,nk}$
- pressure* $P = -(\partial U / \partial V)_{S,nk} = -(\partial A / \partial V)_{T,nk}$
- volume $V = (\partial H / \partial P)_{S,nk} = (\partial G / \partial P)_{T,nk}$
- entropy $S = -(\partial A / \partial T)_{V,nk} = -(\partial G / \partial T)_{P,nk}$

- *when S is constant, the process is called 'isentropic'

These form a sub-set of the Maxwell relations.

Summary of the state functions

- It was shown earlier that the change of internal energy (U) can be expressed as:

$$dU = TdS - PdV$$

- With our focus on the chemical equilibria, we get the relations between the key variables from their definitions as:
 - $H = U + PV$ or in differential form $dH = TdS + VdP$
 - $A = U - TS$ or in differential form $dA = -SdT - PdV$
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Maxwell relations

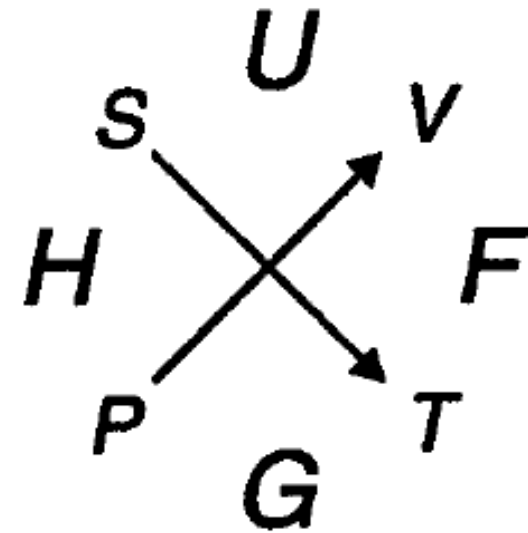
The general correlation for state variables applied to the above equations of internal energy (U), enthalpy (H), Helmholtz (A or F) and Gibbs energy (G) gives us the so-called Maxwell relations:

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V$$

$$(\partial T / \partial P)_S = (\partial V / \partial S)_P$$

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V$$

$$(\partial S / \partial P)_T = -(\partial V / \partial T)_P$$

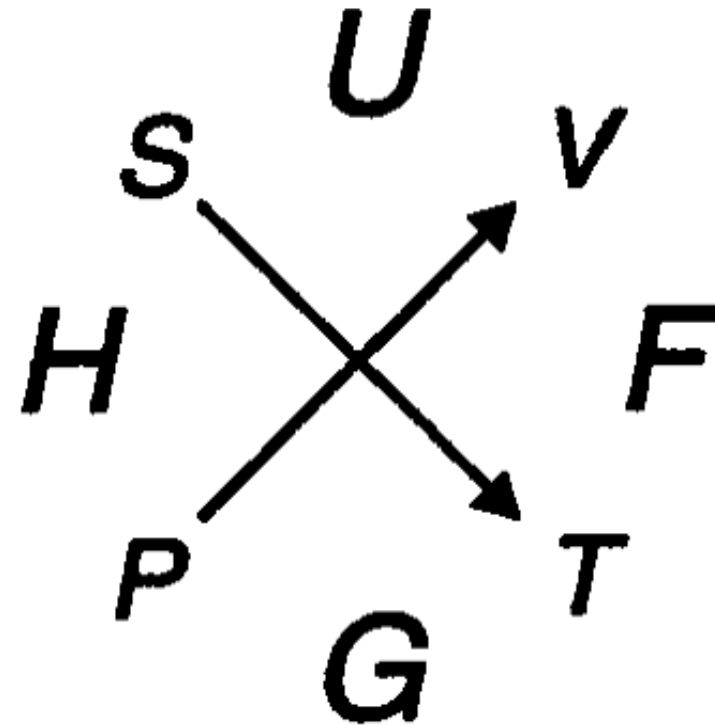


Maxwell relations

Energy (U, H, F or G)

Each energy is flanked by its two most important natural variables

Conjugate variables are in opposite ends of diagonals

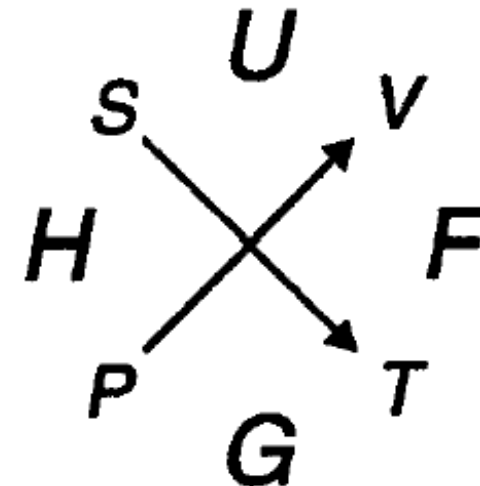


Maxwell relations

Partial derivatives:

Partial derivative of H with respect to P at constant S is $+V$ (*direction of arrow*)

Partial derivative of G with respect to T at constant P is $-S$ (*opposite the arrow*)



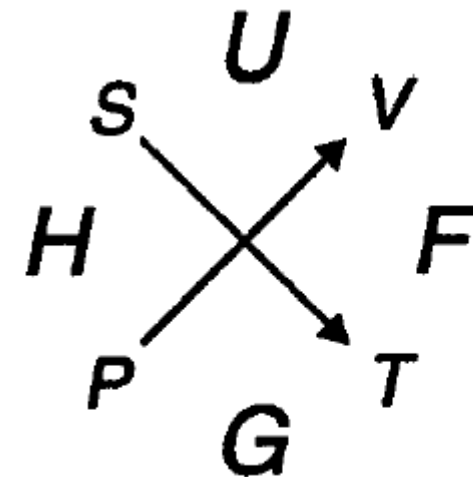
Maxwell relations

Thermodynamic variables:

For any energy take partial derivatives of its natural variables and multiply by their conjugative variables and positive signs along the arrow.

dH is $+V$ times dP plus $+T$ times dS

dG is $-S$ times dT plus $+V$ times dP



Maxwell relations

Maxwell relations:

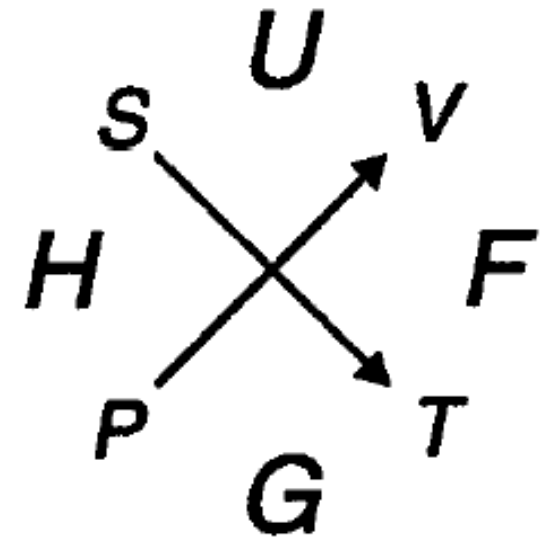
Use no energies, only S, V, T and P

Start from one, go clockwise or counterclockwise

Partial derivative of T with respect to V at constant S and partial derivative of P with respect to S at constant V have opposite signs.

P at arrow start, T at end

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V$$



Impact of pressure on properties of substances - enthalpy

- The pressure dependence derived above for enthalpy in the isothermic processes gives us in the closed systems:

$$dH = (\partial H / \partial P)_T dP.$$

- Combining that with $dH = TdS + VdP$ gives for the pressure dependence of enthalpy

$$(\partial H / \partial P)_T = T(\partial S / \partial P)_T + V.$$

That is modified by Maxwell relation $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$ as

$$(\partial H / \partial P)_T = -T(\partial V / \partial T)_P + V.$$

... continues

- By definition, the isobaric coefficient of expansion α described earlier is

$$\alpha = 1/V(\partial V/\partial T)_P$$

- Inserting to the equation obtained above we get

$$(\partial H/\partial P)_T = -T\alpha V + V = V(1-\alpha T).$$

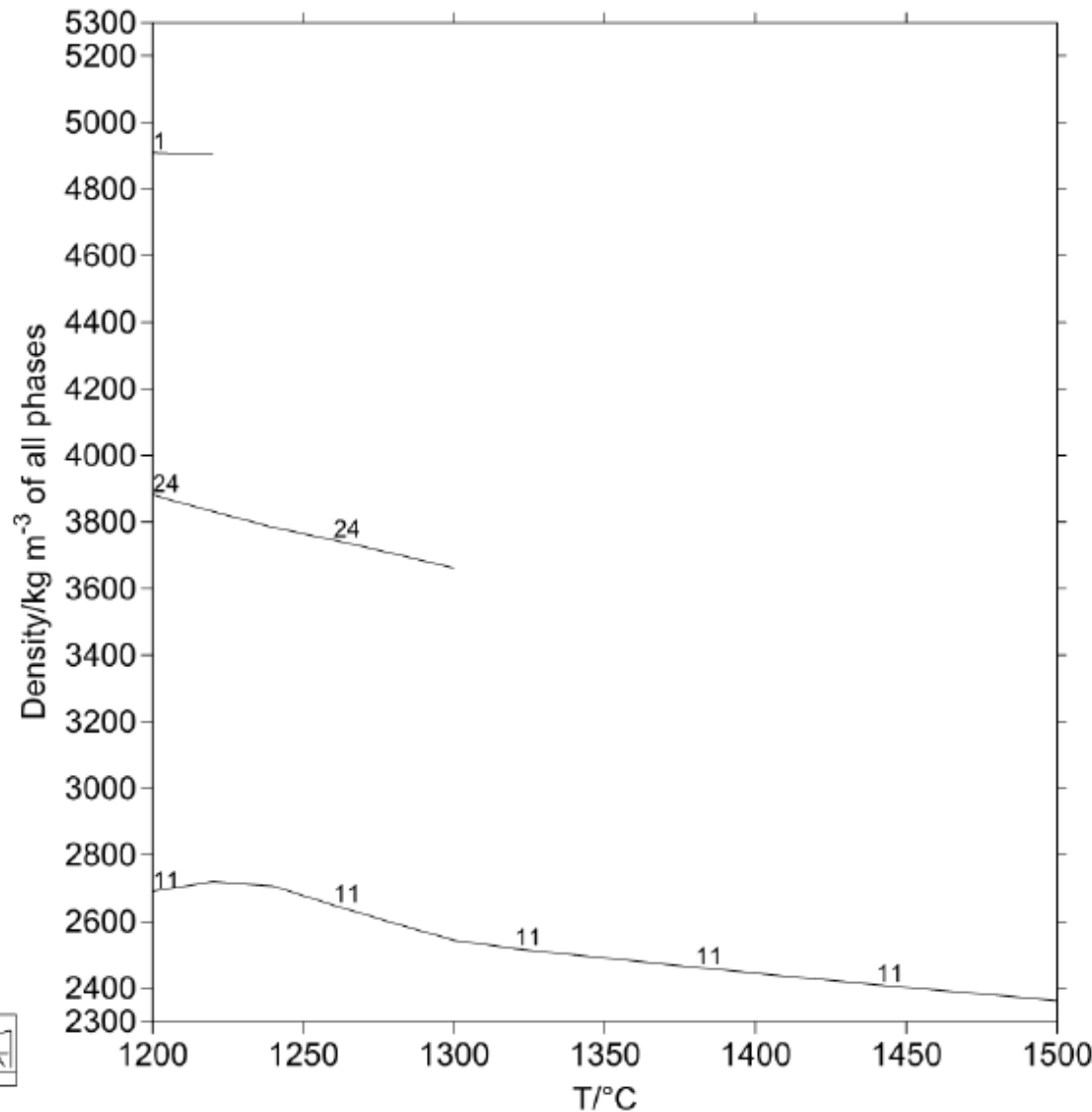
- In isothermal conditions the process in terms of pressure $P_1 \rightarrow P_2$ can be written as

$$\Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} V \cdot (1 - \alpha T) dP.$$

- Thus the molar **volume of a substance (and density) is connected with the pressure dependence of its enthalpy.**
- This feature is useful in practical process calculations, e.g. in precipitation processes.

... continues

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KEY	
1 SPINEL	2-SPINEL
3-CAF2	4-CA2
5-CA	6-C12A7
7-CA6	8-CF
9-C2F	10-C3A
11 LIQUID_OXIDE	12-LIQUID_OXIDE
13-MELILITE	14-MELLITE
15-CLINOPYROXENE	
16-CLINOPYROXENE	
17-C3A2M	
18-PLAGIOCLASE_H	
19-CORDIERITE	20-AF
21-CORUNDUM	22-CORUNDUM
23-MULLITE	24 OLIVINE
25-OLIVINE	
26-ORTHOPYROXENE	
27-HALITE	28-HALITE
29-CWF	30-CF2
31-CW3F	32-C4WF4
33-C4WF8	34-WOLLASTONITE
35-ALPHA_PRIME_C2S	
36-MERWINITE	37-BREDIGITE
38-ALPHA_C2S	
39-PROTOPYROXENE	
40-LOWCLINOPYROXENE	
41-PSEUDO_WOLLASTONITE	
42-HATRURITE	43-RANKINITE
44-METAL_LIQUID	45-BCC_A2
46-FCC_A1	47-HCP_A3
48-ALPHA_QUARTZ	49-BETA_QUARTZ
50-CRISTOBALITE	51-TRIDYMIT

CONSTRAINTS	
P/atm=1	
mass(Al2O3)/kg=1	
mass(CaO)/kg=0.5	
mass(FeO)/kg=48.5	
mass(Fe3O4)/kg=15	
mass(MgO)/kg=5	
mass(SiO2)/kg=30	
STEPPED VARIABLE IS:	
T/K	
WARNING IN STAGE=1	
at stop value=1613.15	
WARNING IN STAGE=1	
at stop value=1713.15	
NO. OF WARNINGS=2	
Stage 1	
No. of calculations=16	
No. shown on plot=16	

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Calculated 08:23:23 12-JAN-2008	
Plotted 08:25:24 12-JAN-2008	

14.11.2022

Impact of pressure

on properties of substances - entropy

- The dependence derived above for the pressure contribution of entropy in closed systems is

$$dS = (\partial S / \partial P)_T dP.$$

- By applying the same Maxwell relation as above and the definition of the isothermal **compressibility** we get

$$(\partial S / \partial P)_T = -\alpha V.$$

- Thus, for an isothermal transformation/process we get:

$$\Delta S = S(P_2, T) - S(P_1, T) = - \int_{P_1}^{P_2} \alpha V dP.$$

Molar volume modelling

- Molar volumes of condensed phases $v(T,P)$ can be expressed using the Murnaghan equation (1942).
- At small pressures it follows the theory of elasticity (Hooke's law). The Murnaghan equation has the form:

$$v(T,P) = v(T,0)/[1+n \cdot K(T,0) \cdot P]^{1/n},$$

where $v(T,0)$ is molar volume under zero pressure 0 or 'vacuum' , $K(T,0)$ is the isothermal compressibility in 0 pressure and n is a constant.

- Constant n can be obtained from pressure dependence of the isothermal bulk modulus (in compression) :

$$B(T,P) = B(T,0) + n \cdot P,$$

where $B(T,0)$ is isothermal module of compression 0 in zero pressure and P is the prevailing pressure.