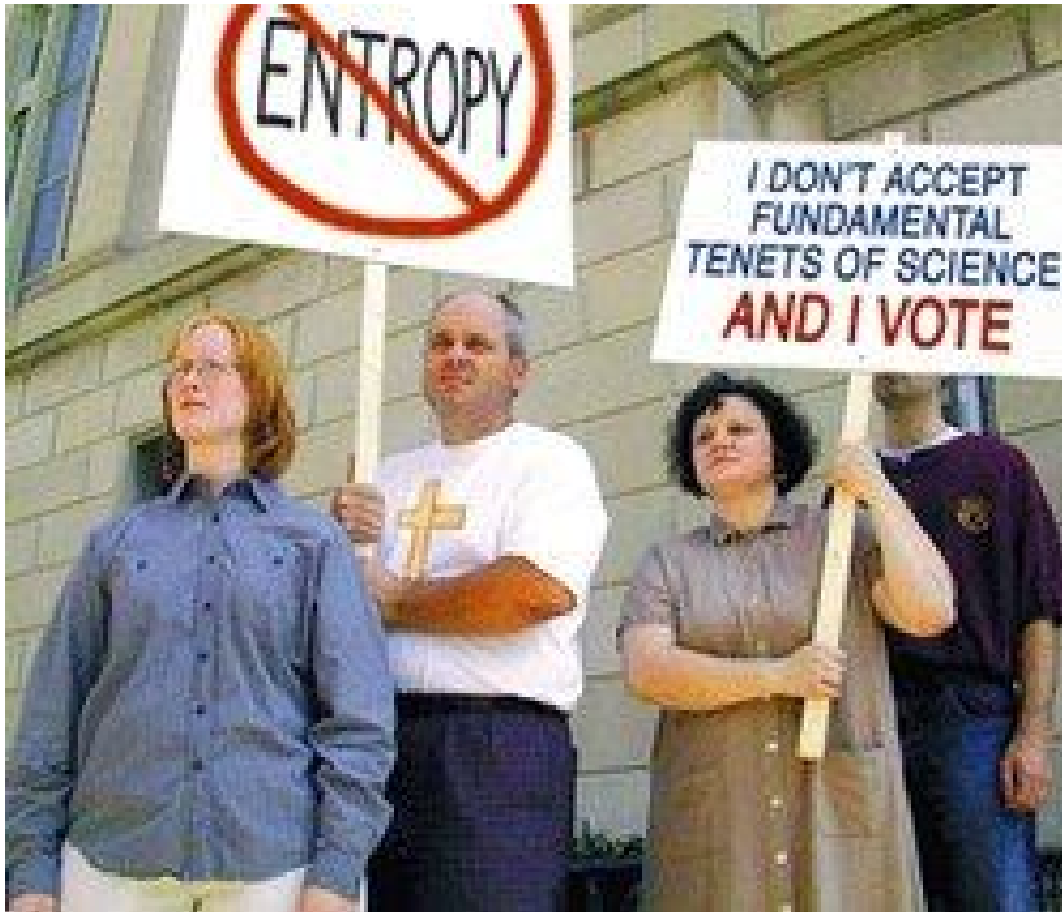# Thermodynamic Aspects of Heterogeneous Catalysis Research

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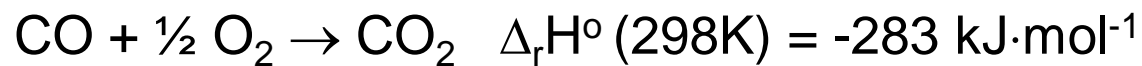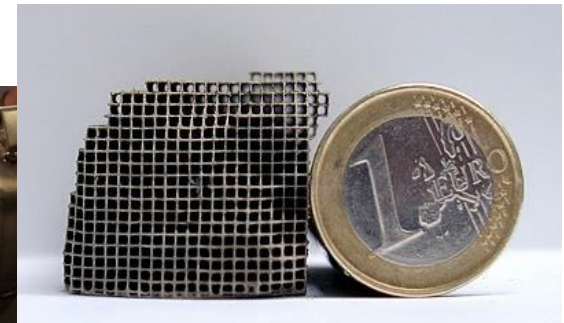
10/26/2012

One way of dealing

with thermodynamics!

or

1. Why does Thermodynamics matters in Catalysis?

2. Thermodynamic Quantities, Concepts and Tools

3. Chemical Equilibrium: Reactor Conversion for a Single Reaction

4. Chemical Equilibrium: Conversion and Selectivity Calculations for Multiple Reactions
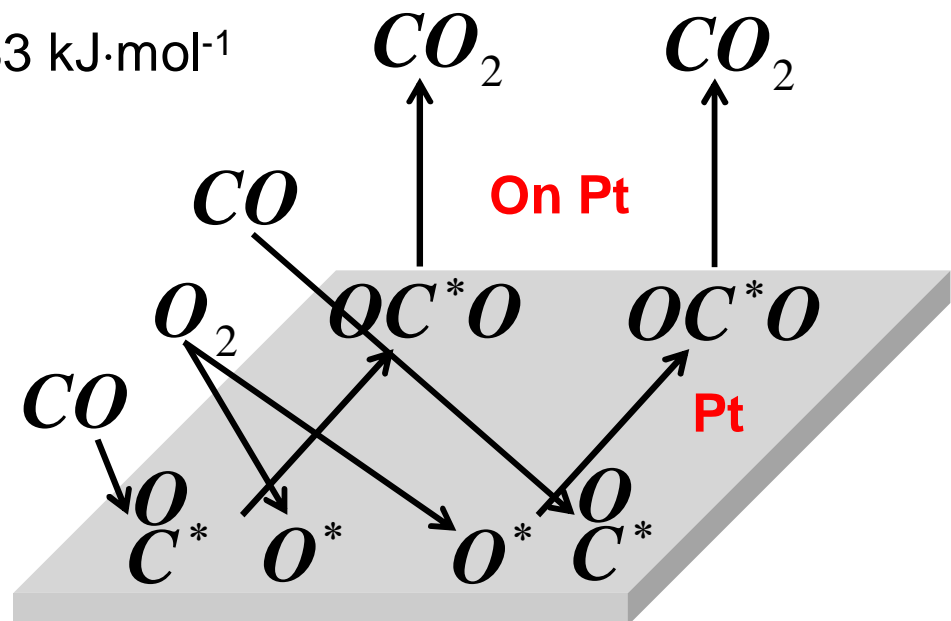
The best-known „catalytic reactor":

One reaction catalyzed by the catalytic converter:

$CO + \frac{1}{2} O_2 \rightarrow CO_2$ $\Delta_r H^o (298K) = -283$ kJ·mol^{-1}

In the gas phase

$$CO + O_2 \qquad \rightarrow CO_2 + O$$
$$CO + O + M \rightarrow CO_2 + M^*$$

CO_2 CO_2

CO **On Pt**

O_2 OC^*O OC^*O

CO **Pt**

O O

C^* O^* O^* C^*

Energetics of CO oxidation

In the gas phase

$$r \propto \exp\left(-\frac{E^{\ddagger}}{RT}\right)$$

$CO(g) + O(g)$

$E^{\ddagger}$

249

$CO(g) + \frac{1}{2}O_2(g)$

259

$E^{\ddagger}$

105

$CO_{ads} + O_{ads}$

$\ddagger$

$\Delta H = 283$

$CO_2(g)$

$CO_{2\ ads}$

~21

On Pt

5

Kinetics

$$-r_A = k(T)C_A(T)$$

T

Equilibrium

$$\ln K = -\frac{\Delta_R G^0}{RT}$$

$$[A^*] = \frac{K_{ads}[A][*]_0}{1 + K_{ads}[A]}$$

Transport

$$\vec{J}_A = -D_{AB}(T)\nabla C_A(T)$$

$$v = v_0 \frac{F_T}{F_{T0}} \frac{p_0}{p} \frac{T}{T_0}$$

Thermodynamics matters in Catalysis because

➢ Thermodynamics determines the maximum extent of any given reaction

➢ The reaction rate decreases with $A \leftrightarrow B$ $\quad -r_A = k_f \left(C_A - \dfrac{C_B}{K_C} \right)$ approach to thermodynamic equilibrium

➢ Heat release or uptake by chemical reactions leads to complex non-isothermal reactor behavior

macroscopic

➢ Adsorption/Desorption thermodynamics determines the concentration of adsorbed species and in turn the rate of surface reactions (e.g. Langmuir Hinshelwood rate expressions)

➢ The kinetics of elementary steps are related to their thermodynamics

microscopic

$$k_i = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_i^{\ddagger}}{k_B T}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S_i^{\ddagger}}{k_B}\right) \exp\left(\frac{-\Delta H_i^{\ddagger}}{k_B T}\right)$$

Equilibrium Conversion and Selectivity
Calculations for Multiple Reactions
(Examples)

Consequences for Reactor Design (Examples)

Chemical Conversion for a Single Reaction (Example)

Chemical Equilibrium and Law of Mass Action

Chemical Potential µ

Clausius Inequality and Gibbs Free Energy G

Entropy S and Second Law of TD

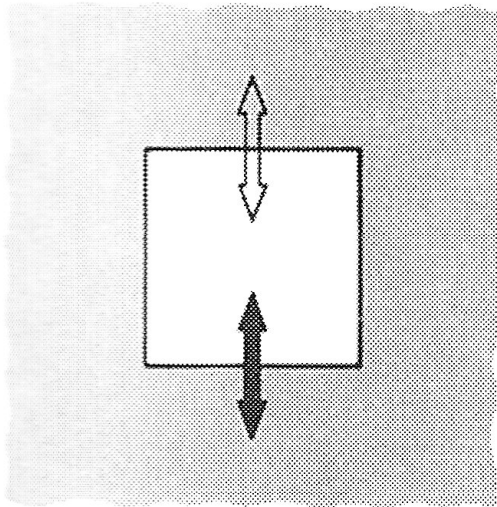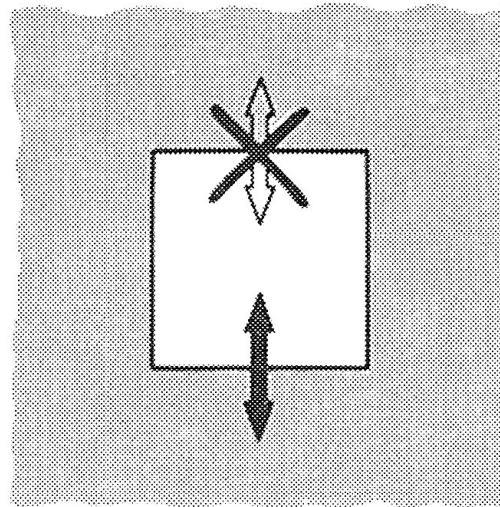First Law of TD, U, H, C_V, C_p

Quantities, Concepts and Tools

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2.1) Systems in Thermodynamics
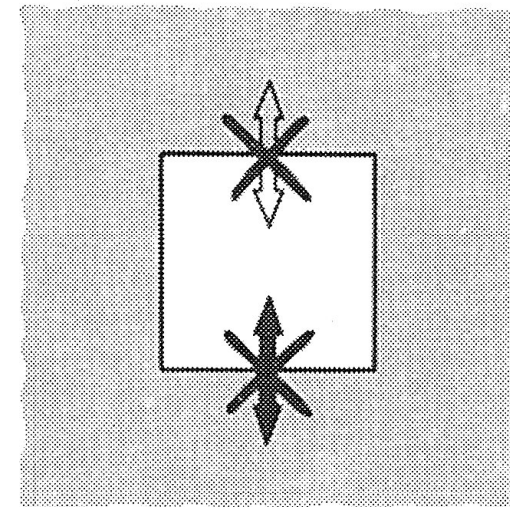
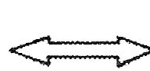| open system | closed system | isolated system |

System   Surroundings ⟺ Exchange of Matter   ⟷ Exchange of Energy

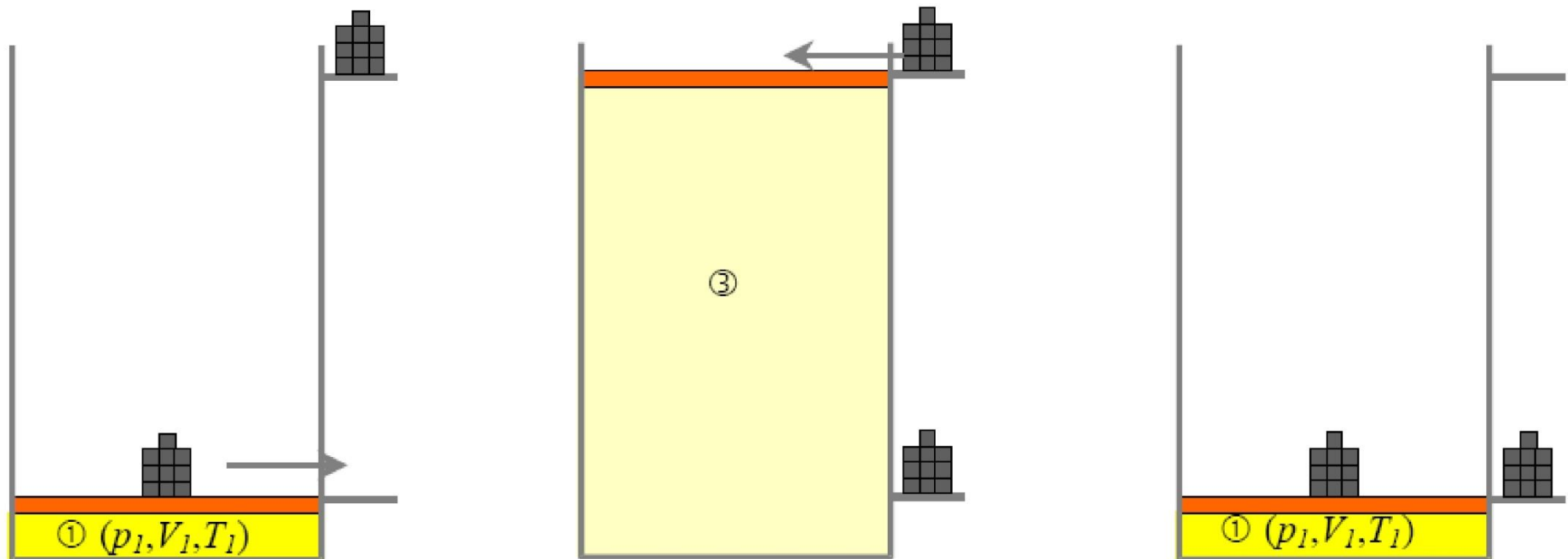| e.g. a heated flow reactor | e.g. an autoclave | e.g. a thermos bottle or the universe |

2.2) Processes

Irreversible Processes

2.2) Processes

Reversible Processes

$$N \cdot \left(\frac{m_{gas}}{N}\right)$$

① (p_1, V_1, T_1)

②

③

① (p_1, V_1, T_1)
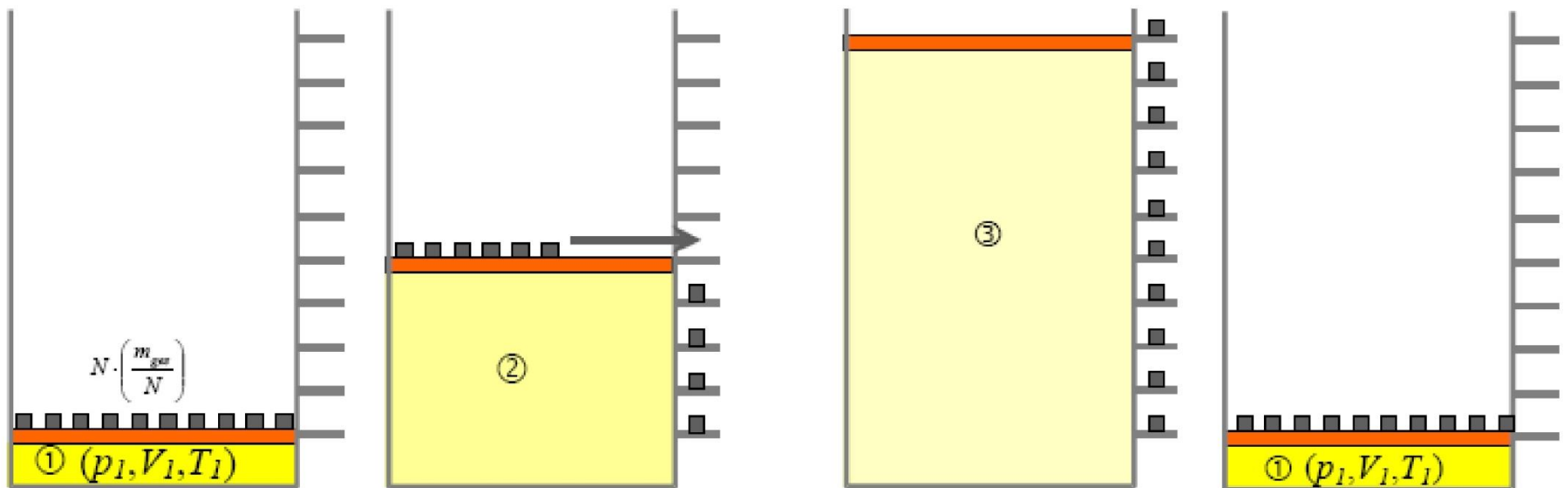
2.3) Important Quantities

Thermodynamic Quantity	Symbol	Intensive or Extensive?	SI Unit
mass	m	extensive	kg
molar mass	M	intensive	$kg \cdot mol^{-1}$
temperature	T	intensive	K
pressure	P, p	intensive	Pa
fugacity	f	intensive	Pa
density	ρ	intensive	$kg \cdot m^{-3}$
volume	V	extensive	m^3
molar volume	$V_m, v, \ldots$	intensive	$m^3 \cdot mol^{-1}$
heat	Q	extensive	J
work	W	extensive	J
inner energy	U	extensive	J
enthalpy	H	extensive	J
free energy, Helmholtz free energy	F, A	extensive	J
free enthalpy, Gibbs free energy	G	extensive	J

2.4) Important Quantities

Thermodynamic Quantity	Symbol	Intensive or Extensive	SI Unit
entropy	S	extensive	$J \cdot K^{-1}$
molare inner energy	U_m, u	intensive	$J \cdot mol^{-1}$
molar enthalpy	H_m, h	intensive	$J \cdot mol^{-1}$
molar free energy	A_m, a, F_m, f	intensive	$J \cdot mol^{-1}$
molar free enthalpy	G_m, g	intensive	$J \cdot mol^{-1}$
chemical potential	μ	intensive	$J \cdot mol^{-1}$
molar entropy	S_m, s	intensive	$J \cdot K^{-1} \cdot mol^{-1}$
heat capacity at constant volume	C_V	extensive	$J \cdot K^{-1}$
heat capacity at constant pressure	C_P	extensive	$J \cdot K^{-1}$
specific heat capacity	$c_{(V,p)}$	intensive	$J \cdot kg^{-1} \cdot K^{-1}$
molar heat capacity	$C_{m(V,p)}, c_{m(V,p)}$	intensive	$J \cdot mol^{-1} \cdot K^{-1}$

2.4.1) Internal Energy U in J

$$U = U_{trans} + U_{vib} + U_{rot} + U_{chem} + U_{nuc} + U_{el} + U_{magn} + ...$$

$$U = f(T, V, n_1, n_2, ..., n_k)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n_j} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n_j} dV + \left(\frac{\partial U}{\partial n_1}\right)_{T,V,n_{j\neq 1}} dn_1 + ... + \left(\frac{\partial U}{\partial n_k}\right)_{T,V,n_{j\neq k}} dn_k$$

C_V (internal pressure π)

0 for ideal gases

$$dU = \delta W + \delta Q$$

First Law of Thermodynamics:

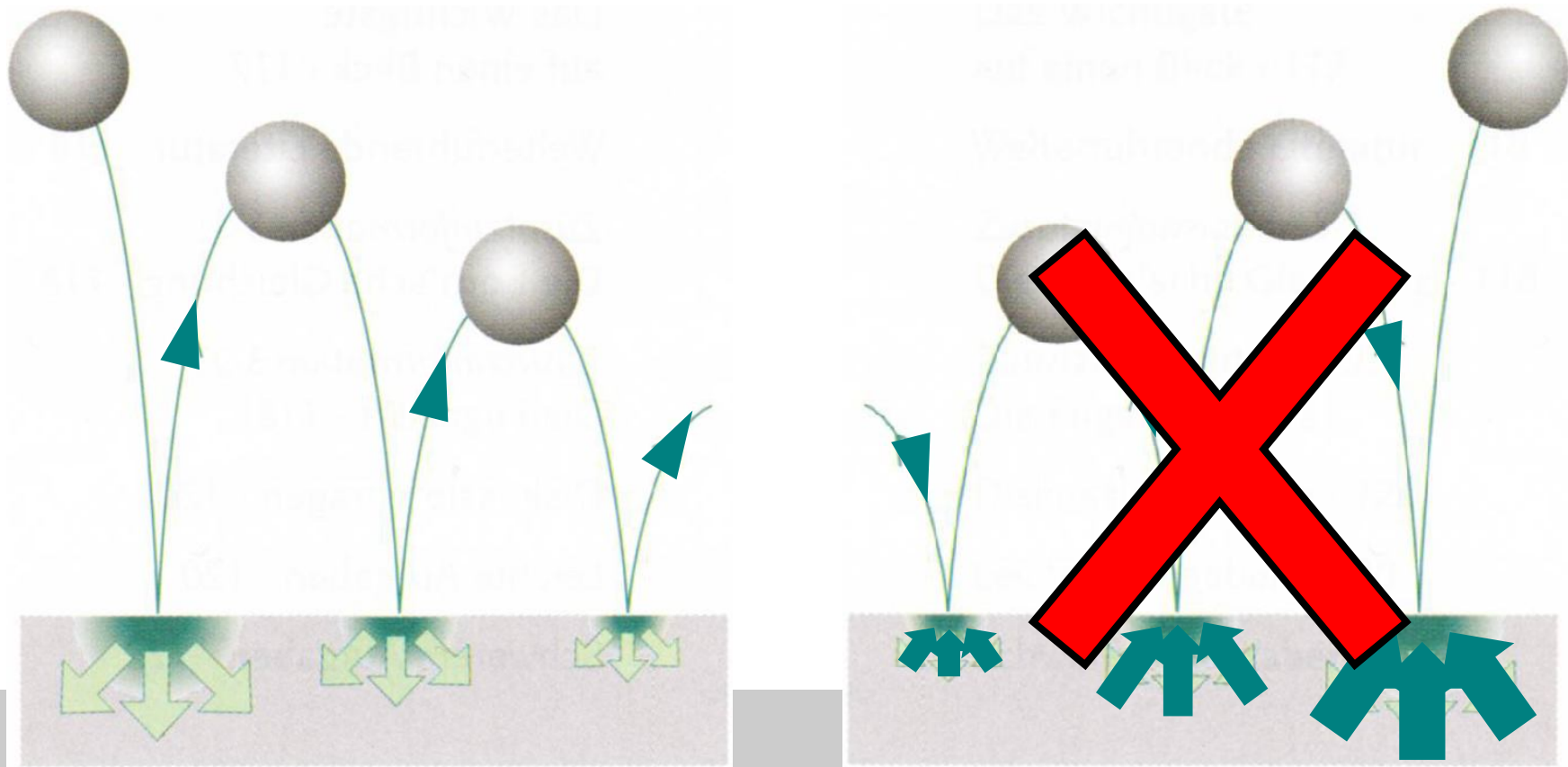$$\Delta U = Q + W$$

2.4.2) Internal Energy U in J

The First Law of Thermodynamics is important for describing non-isothermal reactors (energy balance) but says nothing about the direction of a physical or chemical process!

$$\Delta U = Q + W$$

2.4.3) Enthalpy H in J

$$(dU)_p = \delta Q_p - pdV$$

$$U_{II} - U_I = Q_p - p(V_{II} - V_I)$$

$$Q_p = (U_{II} + pV_{II}) - (U_I + pV_I)$$

$$H = U + pV$$

$$Q_p = H_{II} - H_I$$

weight

area
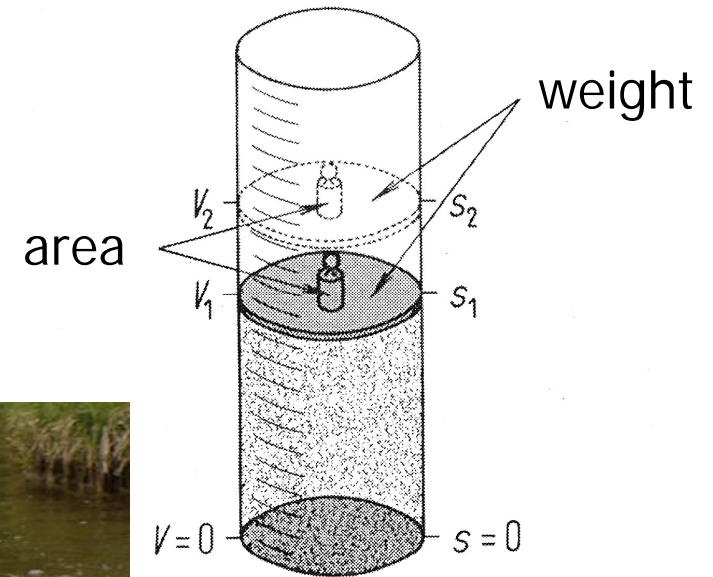
$$\boldsymbol{H = H(T, p, n_1, n_2, ..., n_k)}$$

$$\boldsymbol{dH = \left(\frac{\partial H}{\partial T}\right)_{p,n_j} dT + \left(\frac{\partial H}{\partial p}\right)_{T,n_j} dp + \left(\frac{\partial H}{\partial n_1}\right)_{p,T,n_{j\neq1}} dn_1 + ...}$$

$$\boldsymbol{C_p}$$ (isothermer drosseleffekt ε in m^3) 0 for ideal gases

2.4.3) Enthalpy H in J

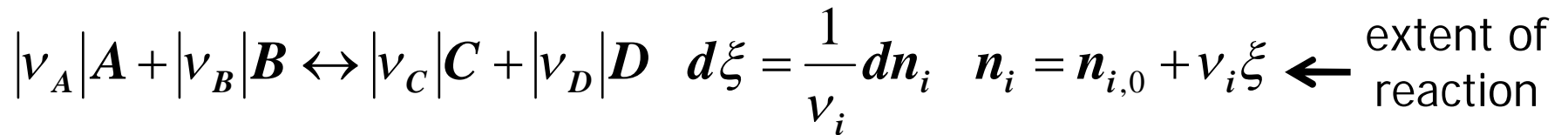$$|v_A|A + |v_B|B \leftrightarrow |v_C|C + |v_D|D \quad d\xi = \frac{1}{v_i}dn_i \quad n_i = n_{i,0} + v_i\xi \leftarrow \text{extent of reaction}$$

$$\left(\frac{\partial H}{\partial \xi}\right)_{p,T} = \Delta H \quad \text{enthalpy of reaction} \quad \Delta H = \sum_i v_i H_i \quad \text{Hess Law}$$
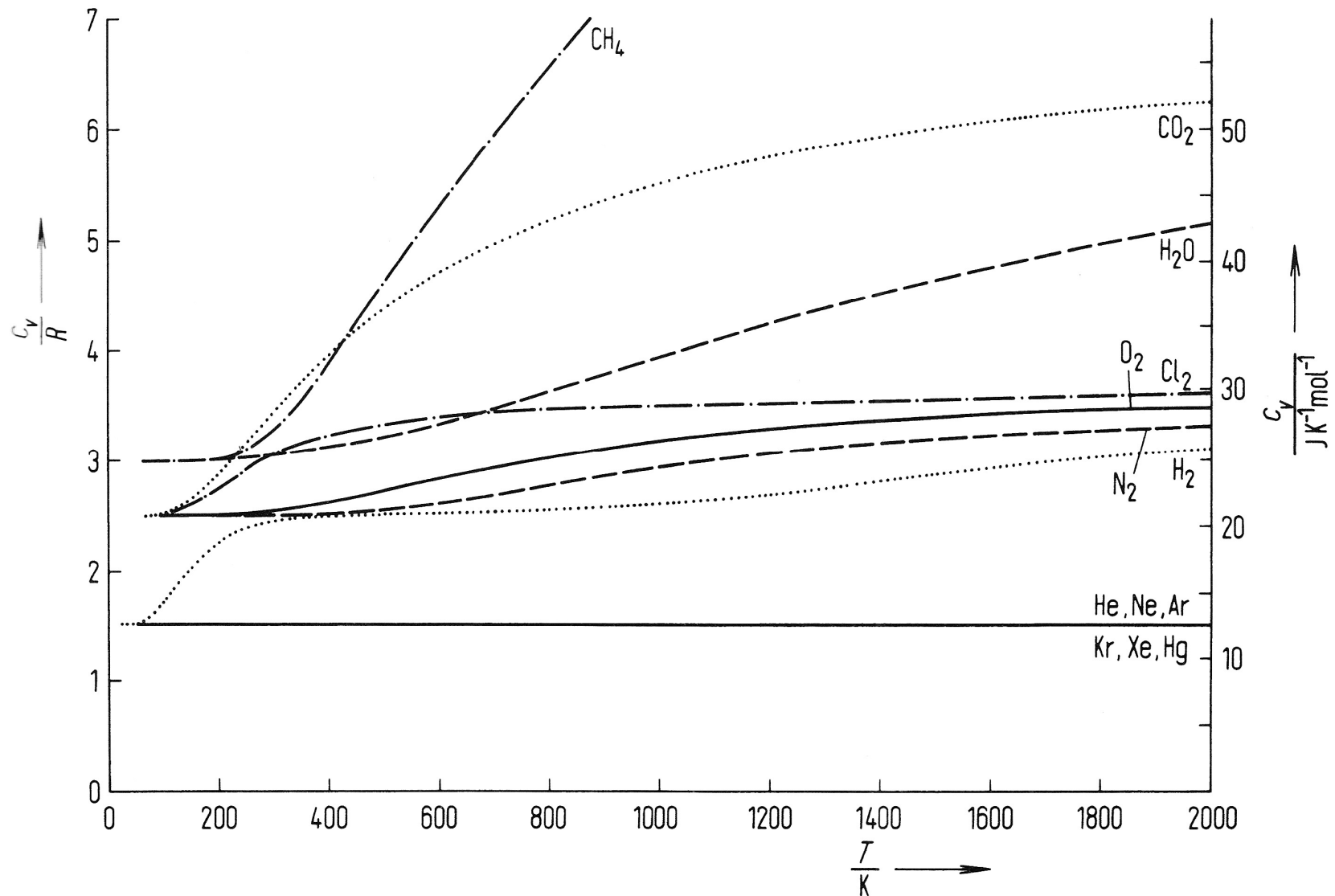
example: $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \quad \Delta H = -\frac{1}{2}\cdot H_{N_2} + \left(-\frac{3}{2}\right)\cdot H_{H_2} + 1\cdot H_{NH_3}$

The standard enthalpy of formation $\Delta H_f°$ or standard heat of formation of a compound is the change of enthalpy that accompanies the formation of 1 mole of the compound from its elements, with all substances in their standard states. The standard state of a gas is the (hypothetical) ideal gas at 1bar and 298.15K. For liquids and solids it is the pure substance at 1bar and 298.15K.

$$H_{NH_3} \equiv \Delta H_f°(NH_3) = -\frac{1}{2}\cdot H_{N_2} + \left(-\frac{3}{2}\right)\cdot H_{H_2} + 1\cdot H_{NH_3}$$

2.4.4) Heat capacities C_V, C_p in J/K

for ideal gases $$C_{p,m} = C_{V,m} + R$$

2.4.4) Heat capacities C_V, C_p in J/K

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \quad \Delta_r H^\circ = -45.9\frac{kJ}{mol} \quad \Delta_r C_p = \sum_i \nu_i C_{pi} = -22.186\frac{J}{mol \cdot K}$$

$T = 298.15K$
$p = 1bar$
$\frac{1}{2}N_2 + \frac{3}{2}H_2$

$T = 298.15K$
$p = 1bar$
$1NH_3$
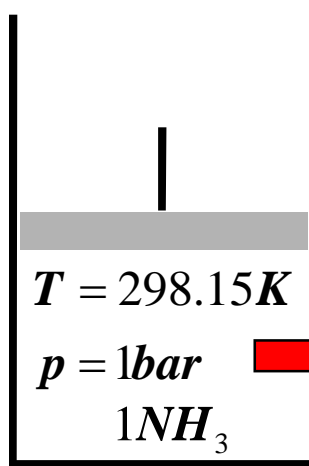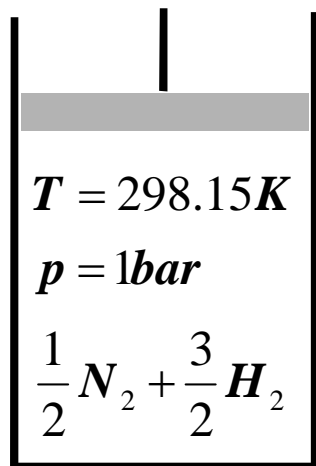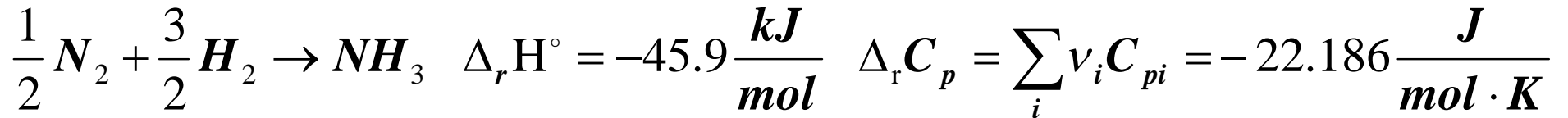
$45.9\frac{kJ}{mol}$

Kirchhoff's law

$$\left(\frac{\partial(\Delta_r H)}{\partial T}\right)_p = \Delta_r C_p$$

$T = 400K$
$p = 1bar$
$\frac{1}{2}N_2 + \frac{3}{2}H_2$

$T = 400K$
$p = 1bar$
$1NH_3$

$\approx 48.2\frac{kJ}{mol}$

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT$$
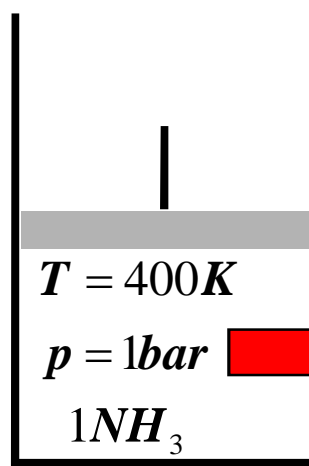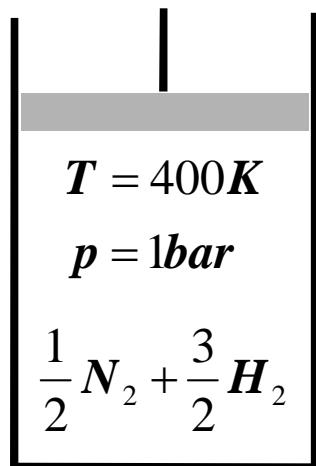
2.4.5) Entropy
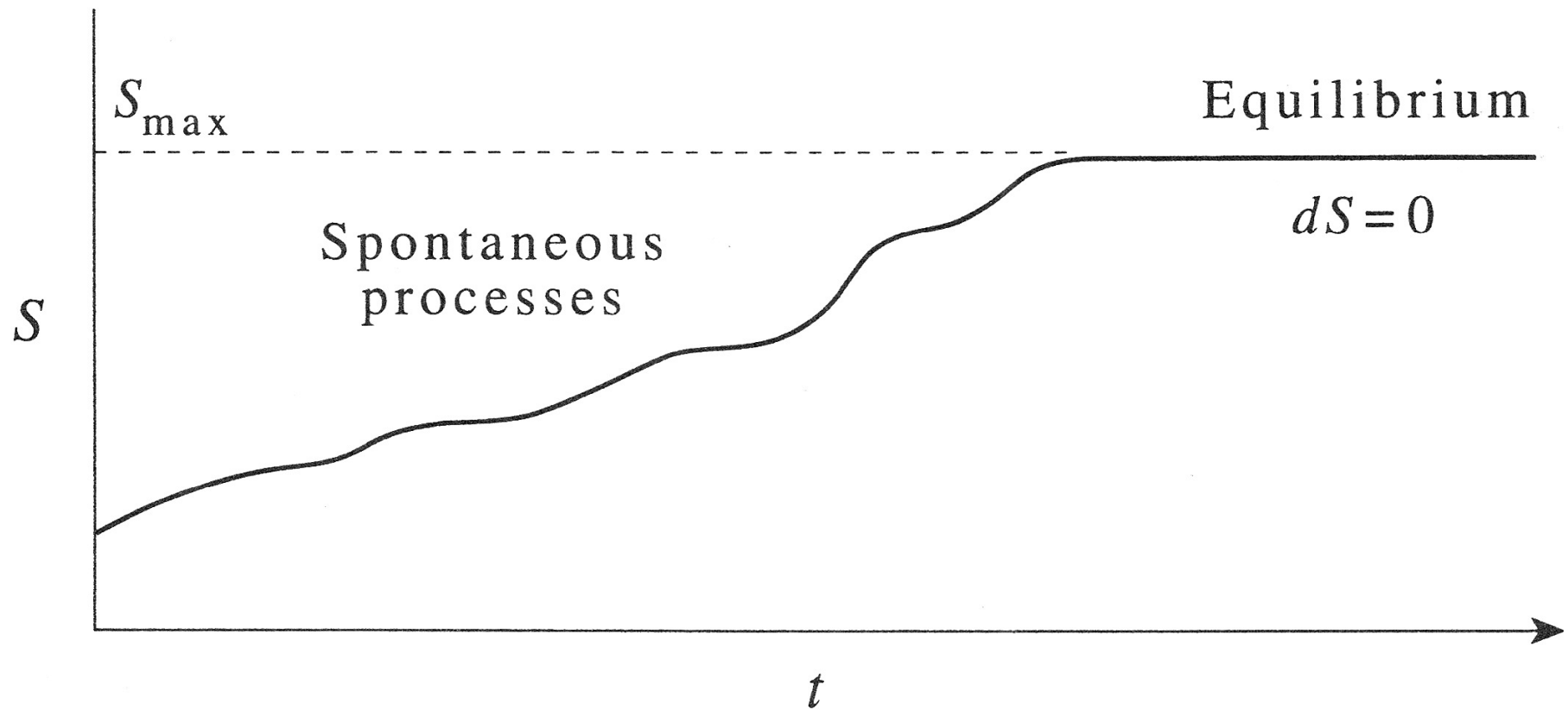
Example: 3 Molecules (A,B,C) distributed among 4 energy states
($\varepsilon_0=0$, $\varepsilon_1= \varepsilon_1$, $\varepsilon_2=2\cdot\varepsilon_1$, $\varepsilon_3=3\cdot\varepsilon_1$) with a total energy of $\varepsilon_{total}=3\cdot\varepsilon_1$ (isolated system)

Energy State	Energy	Macrostate										
$$S = k \cdot \ln W$$		I			II						III	
ε_3	$3\cdot\varepsilon_1$	A	B	C								
ε_2	$2\cdot\varepsilon_1$				C	B	C	A	B	A		
ε_1	$1\cdot\varepsilon_1$				B	C	A	C	A	B	ABC	
ε_0	$0\cdot\varepsilon_1$	BC	AC	AB	A	A	B	B	C	C		
# of Microstates (statistical weight W)		3			6						1	

2.4.5) Entropy

$$dS \geq 0 \quad \text{Second Law of Thermodynamics}$$

2.4.5) Entropy

irreversible
process

reversible
process
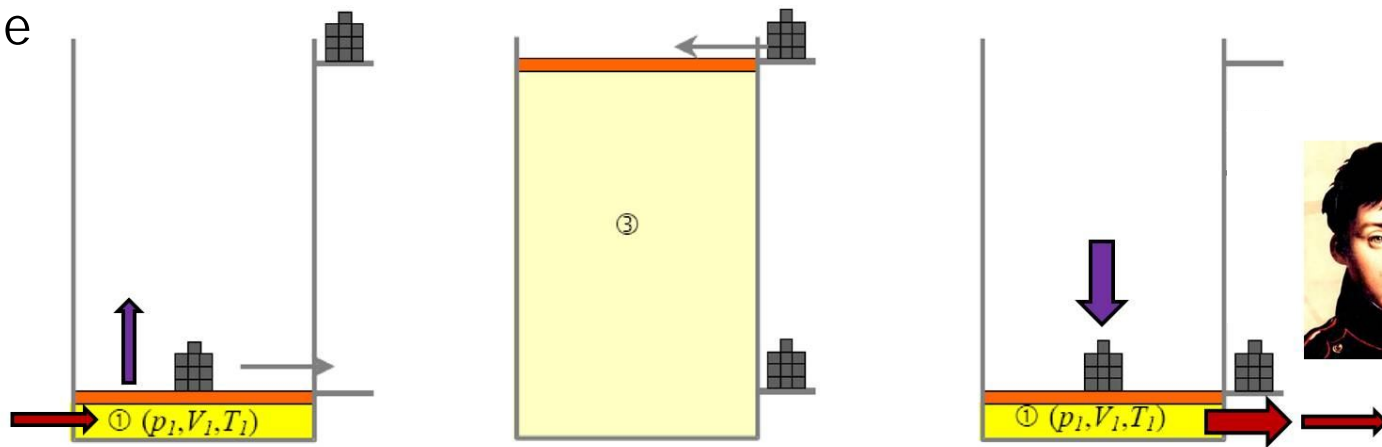
$$\eta = 1 - \frac{T_{low}}{T_{high}}$$

Sadi
Carnot

Q ➡ **W** ➡

① (p_1, V_1, T_1)

③

① (p_1, V_1, T_1)

① (p_1, V_1, T_1)

②

③

① (p_1, V_1, T_1)
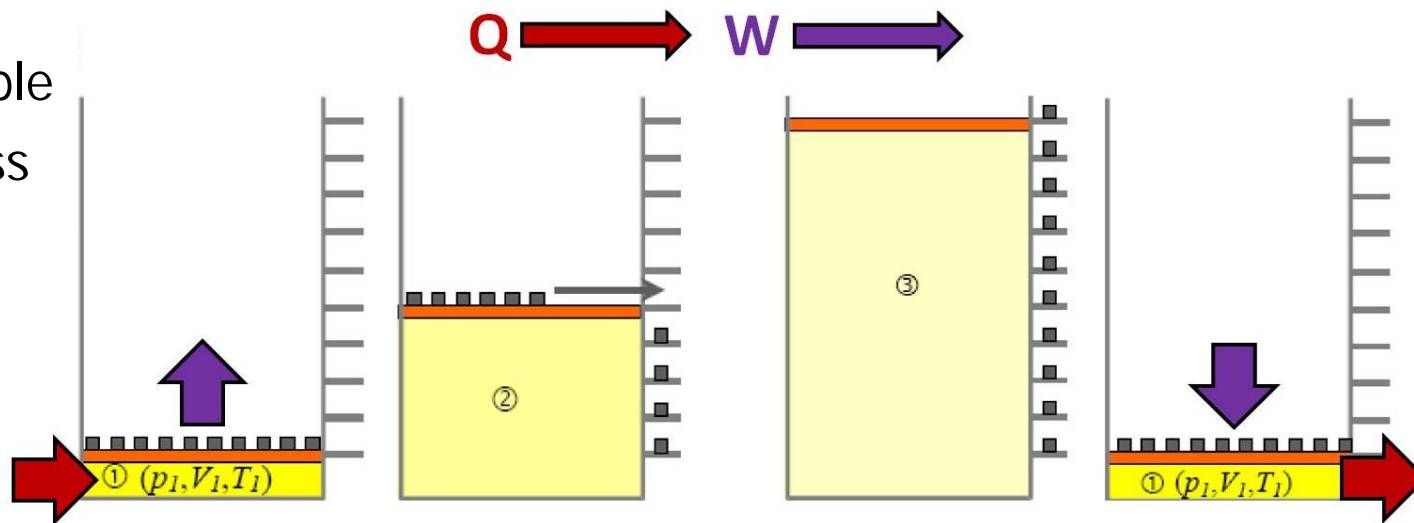
2.4.5) Entropy

Rudolph Clausius
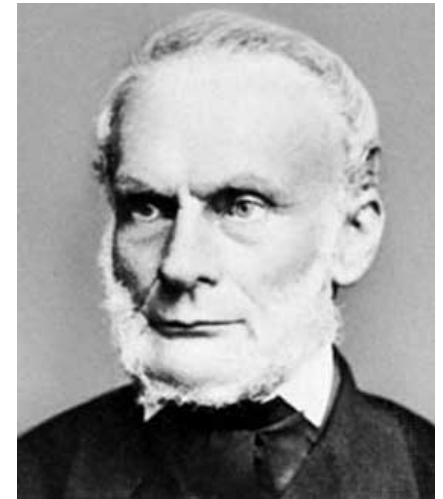
$$\frac{dQ_{rev}}{T} = dS \qquad \oint \frac{dQ_{rev}}{T} = 0 \qquad \oint \frac{dQ_{irrev}}{T} < 0$$

Irreversible

1   2

Reversible
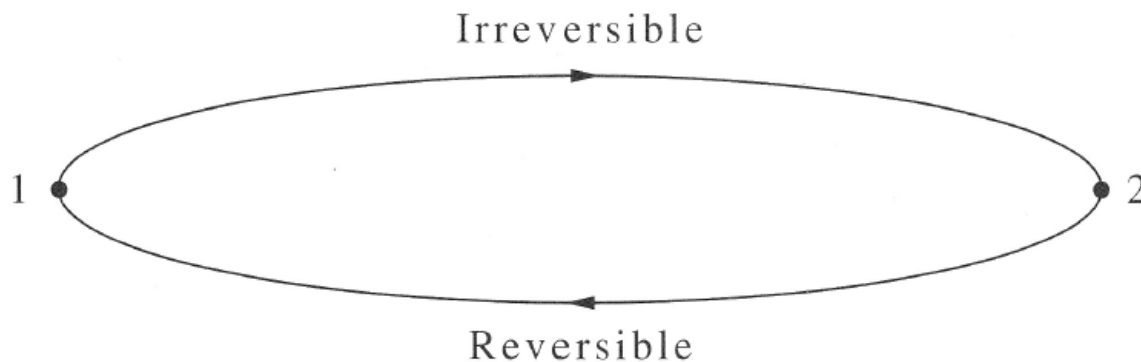
$$\oint_{irrev} \frac{dQ}{T} = \int_1^2 \frac{dQ_{irr}}{T} + \int_2^1 \frac{dQ_{rev}}{T} < 0 \implies \oint_{irrev} \frac{dQ}{T} = \int_1^2 \frac{dQ_{irr}}{T} + \int_2^1 dS < 0$$

Clausius Inequality

$$\boxed{dS \geq \frac{dQ}{T}} \impliedby \int_1^2 \frac{dQ_{irr}}{T} < \int_1^2 dS$$

2.4.6) Helmholtz Free Energy (Free Energy) and
Gibbs Free Energy (Free Enthalpy)

Clausius Inequality
$$dS \geq \frac{dQ}{T} \Rightarrow 0 \geq dQ - TdS$$

$$(\delta Q)_V = dU$$
$$(\delta Q)_p = dH$$

spontaneous process at constant volume $\qquad dU - TdS < 0$

spontaneous process at constant pressure $\qquad dH - TdS < 0$

Helmholtz Free Energy (Free Energy):
$$A = U - TS$$
$$dA = dU - TdS$$

Gibbs Free Energy (Free Enthalpy):
$$G = H - TS$$
$$dG = dH - TdS$$

2.4.7) Dependencies of G by Combining the First and Second Law of Thermodynamics

$$G = H - TS$$

$$dU = \delta Q + \delta W = \delta Q_{rev} + \delta W_{rev} = TdS - pdV$$

$$H = U + pV \Rightarrow dH = dU + pdV + Vdp$$

$$dH = TdS - pdV + pdV + Vdp = TdS + Vdp$$

$$dG = dH - TdS - SdT = TdS + Vdp - TdS - SdT = VdP - SdT$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

2.4.8) Gibbs Free Energy in Mixtures and the Chemical Potential

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_{j\neq 1}} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_{j\neq 2}} dn_2 + ...+ \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} dn_i$$

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

T,p=const.

chemical potential of i

$\mu_{i,A}$ $\qquad$ $\mu'_{i,A}$

spontan
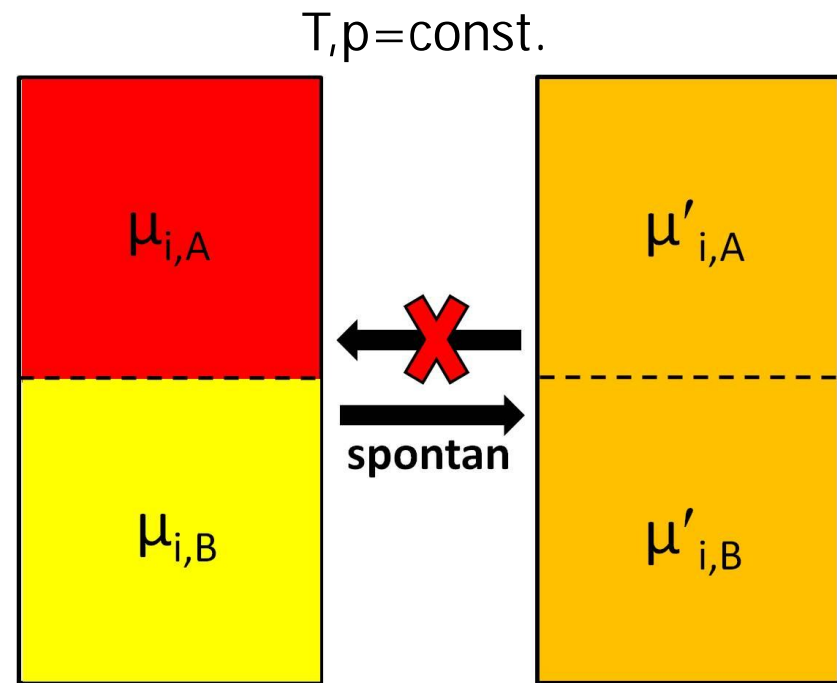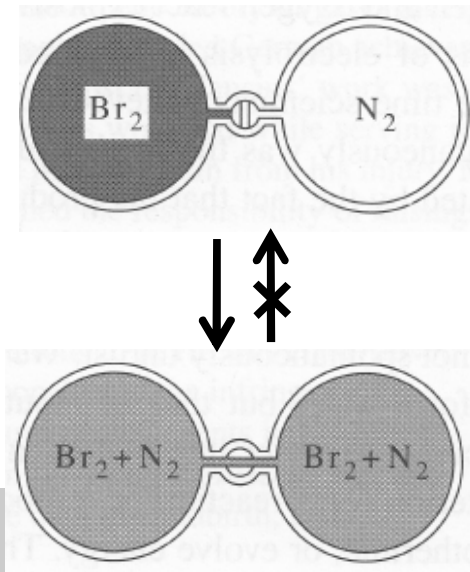
$\mu_{i,B}$ $\qquad$ $\mu'_{i,B}$

$$dG = \mu_{i,A}dn_{i,A} + \mu_{i,B}dn_{i,B}$$
$$= \left(\mu_{i,B} - \mu_{i,A}\right)dn_{i,B} < 0$$

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2.4.8) Gibbs Free Energy in Mixtures and the Chemical Potential

$$\left(\frac{\partial \mu_i}{\partial T}\right)_p = \left(\frac{\partial(-S)}{\partial n_i}\right)_{p,T,n_{j\neq i}} = -S_{m,i}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = \left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{j\neq i}} = V_{m,i}$$

Example: pure ideal gas

$$pV = nRT \Rightarrow V_m = \frac{V}{n} = \frac{RT}{p}$$

$$\int_{p1}^{p2} \mu^{id} = \int_{p1}^{p2} V_m^{id} dp \Rightarrow$$

$$\mu^{id}(p_2) = \mu^{id}(p_1) + RT \int_{p1}^{p2} \frac{1}{p} dp = \mu^{id}(p_1) + RT \ln \frac{p_2}{p_1}$$

2.4.8) Gibbs Free Energy in Mixtures and the Chemical Potential

$$\mu_i(p, T) = \mu_i^*(p_i, T)$$

Membrane permeable for i
(e.g. Pd and i=H_2)

for ideal gaseous and liquid mixtures

$$\mu_i(p, T) = \mu_i^*(p, T) + RT \ln \frac{p_i}{p}$$

$$= \mu_i^*(p, T) + RT \ln x_i$$

for real systems

$$\mu_i(p, T) = \mu_i^*(p, T) + RT \ln a_i$$

$$a_i = f_i \cdot x_i$$

in any case
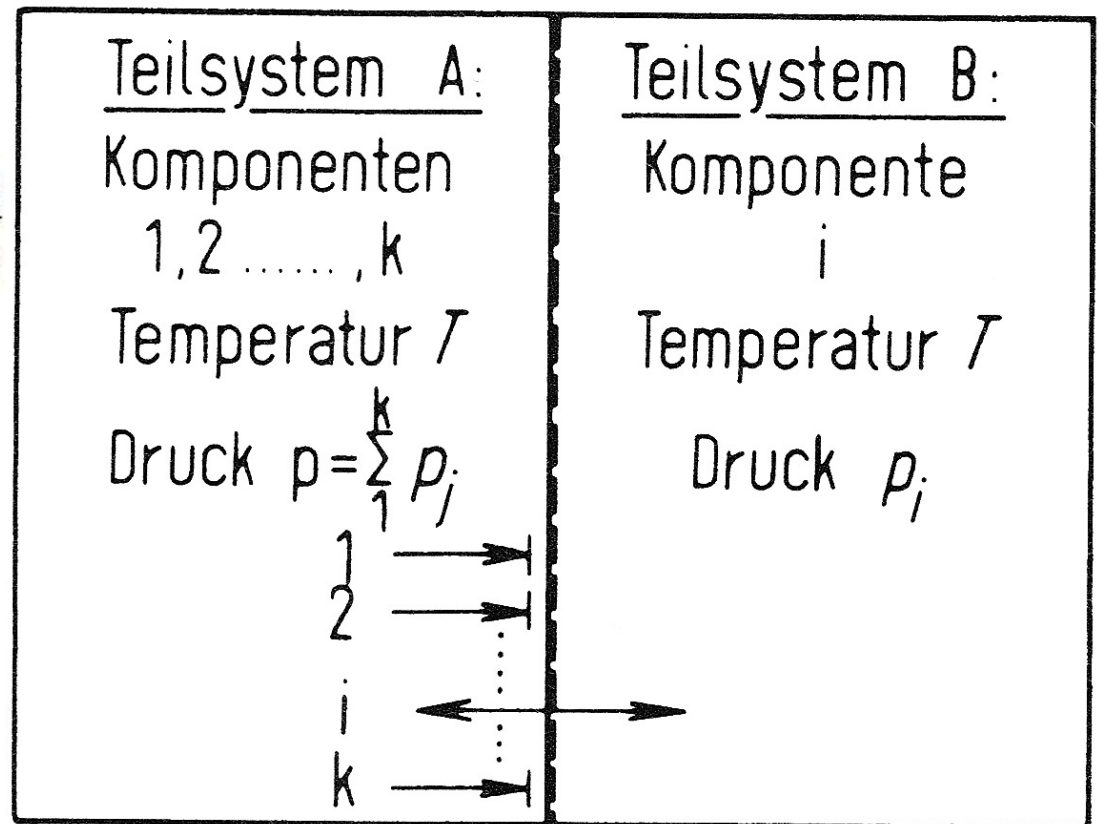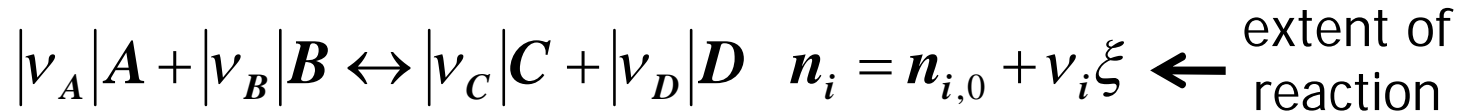
$$\mu_i(p, T) < \mu_i^*(p, T)$$

Teilsystem A:	Teilsystem B:
Komponenten 1,2 ...... , k	Komponente i
Temperatur T	Temperatur T
Druck $p = \sum_1^k p_j$	Druck p_i

1 →
2 →
i ←
k →

2.5)   Chemical Equilibrium

$$|v_A|A + |v_B|B \leftrightarrow |v_C|C + |v_D|D \quad n_i = n_{i,0} + v_i \xi \quad \leftarrow \begin{array}{l}\text{extent of} \\ \text{reaction}\end{array}$$

$$dn_i = v_i d\xi$$

$$(dG)_{p,T} = \sum \mu_i dn_i = \sum \mu_i v_i d\xi \Rightarrow (\Delta G)_{p,T} = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum v_i \mu_i$$

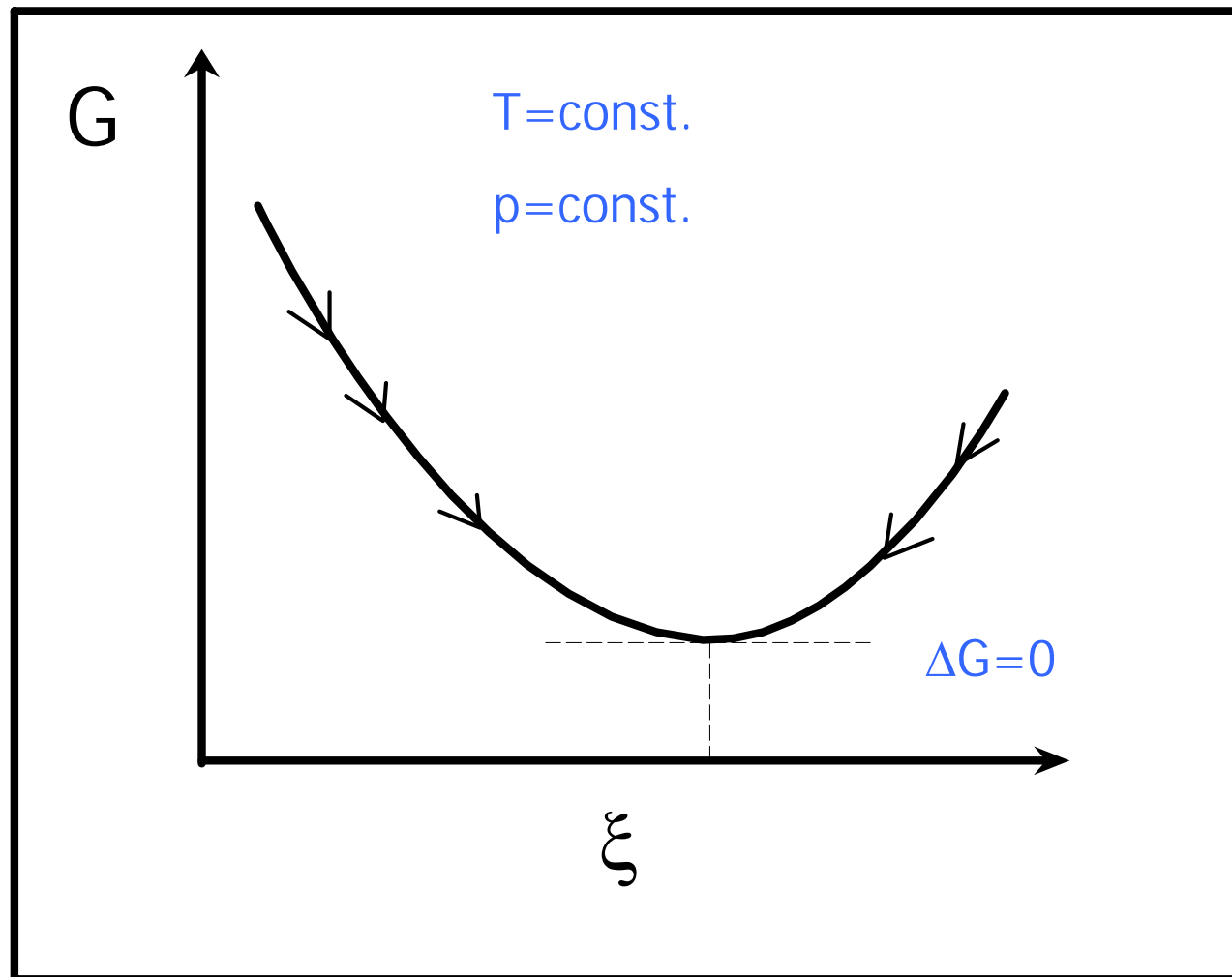in equilibrium $(\Delta G)_{p,T} = 0$

$$\mu_i^{real}(p,T) = \mu_i^0(p,T) + RT \ln a_i \qquad \Delta G = \sum v_i \mu_i^0 + RT \sum v_i \ln a_i$$

$$\Delta G = \sum v_i \mu_i^0 + RT \sum v_i \ln[a_i] = 0$$

2.5)　Chemical Equilibrium

2.5)   Chemical Equilibrium

$$\Delta G = \sum \nu_i \mu_i^0 + RT \sum \nu_i \ln[a_i] = 0$$

$$\Delta G = \Delta G^0 + RT \ln \prod [a_i]^{\nu_i} = 0$$

law of mass action

$$\ln \prod [a_i]^{\nu_i} = -\frac{\Delta G^0}{RT} = \ln K \Rightarrow \boxed{K = \prod [a_i]^{\nu_i}}$$

standard state for all gases is the pure ideal gas at 1bar

activity of
an ideal gas

$$a_i = \frac{p_i}{p^0}$$

$$K = \underbrace{\prod [p_i]^{\nu_i}}_{K_p} \cdot (p^0)^{-\sum \nu_i}$$

2.5)   Chemical Equilibrium

$$K \neq f(p) \leftarrow K = \prod [p_i]^{\nu_i} \cdot (p^0)^{-\sum \nu_i}$$

$$\underbrace{\phantom{\prod [p_i]^{\nu_i}}}_{K_p} \rightarrow K_p \neq f(p)$$

$$K = \prod_i [x_i p]^{\nu_i} (p^\circ)^{-\sum \nu_i} = \prod_i [x_i]^{\nu_i} \cdot \left(\frac{p}{p^\circ}\right)^{\sum \nu_i} = K_x \cdot \left(\frac{p}{p^\circ}\right)^{\sum \nu_i}$$

$$p_i V = n_i RT \Rightarrow p_i = c_i RT \qquad K_x = f(p)$$

$$K = \prod_i [c_i RT]^{\nu_i} (p^\circ)^{-\sum \nu_i} = \prod_i [c_i]^{\nu_i} \cdot \left(\frac{RT}{p^\circ}\right)^{\sum \nu_i} = K_c \cdot \left(\frac{p}{p^\circ}\right)^{\sum \nu_i}$$

$$K_c = f(p)$$

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2.5)   Chemical Equilibrium

Temperature Dependance of K:

Gibbs Helmholtz Equation

$$\left(\frac{\partial \Delta G^0/T}{\partial T}\right)_p = -\frac{\Delta H^0}{T^2} \qquad \Delta G^0(T) = -RT\ln K$$
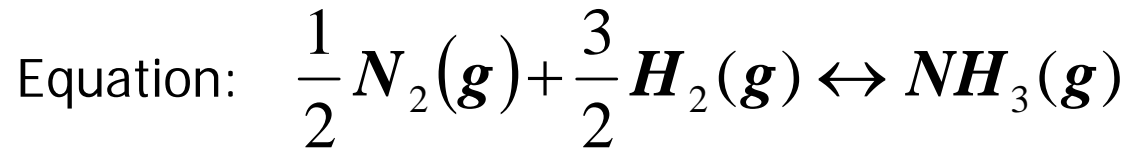
$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^0}{RT^2} \qquad \text{van't Hoff Equation}$$

$$\ln K(T) = \ln K(T_1) + \int_{T_1}^{T} \frac{\Delta H^0(T')dT'}{RT'^2}$$

$$\Delta H^0(T) = \Delta H^0(T_1) + \int_{T_1}^{T} \Delta C_p^0(T')dT'$$

Example: Calculate the maximum NH_3 yield of the Haber-Bosch-Process for $25°C \leq \vartheta \leq 600 °C$ and $1 bar \leq p \leq 500$ bar! Assume a stoichiometric feed and ideal gases for simplicity!

$$\text{Equation:} \quad \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \leftrightarrow NH_3(g)$$

Thermodynamic Data (NIST Chemistry Webbook, CRC Handbook, PC books...):

Species	$\Delta H_f° / kJ·mol^{-1}$	$S° / J·mol^{-1}·K^{-1}$	$C_p° / J·mol^{-1}·K^{-1}$		
			A	B / 10^{-3} K^{-1}	C / 10^{-6} K^{-2}
N_2	0	191.6	24.98	5.912	-0.3376
H_2	0	130.7	29.07	-0.8368	2.012
NH_3	-45.9	192.8	25.93	32.58	-3.046

$$C_p° / J \cdot K^{-1} \cdot mol^{-1} = A + B \cdot T + C \cdot T^2$$

Calculate K for 25°C: $\Delta G° = \Delta H° - T \cdot \Delta S°$ $-\dfrac{\Delta G^0}{RT} = \ln K$

Species	ν_i	$\Delta H_f° / kJ \cdot mol^{-1}$	$S° / J \cdot mol^{-1} \cdot K^{-1}$	$C_p° / J \cdot mol^{-1} \cdot K^{-1}$		
				A	B / 10^{-3} K^{-1}	C / 10^{-6} K^{-2}
N_2	-1/2	0	191.6	24.98	5.912	-0.3376
H_2	-3/2	0	130.7	29.07	-0.8368	2.012
NH_3	1	-45.9	192.8	25.93	32.58	-3.046

$$\Delta H° = \left[-1/2 \cdot 0 + (-3/2) \cdot 0 + 1 \cdot (-45.9) \right] \frac{kJ}{mol} = -45.9 \frac{kJ}{mol}$$

$$\Delta S° = \left[-1/2 \cdot 191.6 + (-3/2) \cdot 130.7 + 1 \cdot 192.8 \right] \frac{J}{mol \cdot K} = -99.05 \frac{J}{mol \cdot K}$$

$$\Delta G° = -45.9 \frac{kJ}{mol} - 298.15 K \cdot \left(-99.05 \cdot 10^{-3} \right) \frac{kJ}{mol \cdot K} = -16.37 \frac{kJ}{mol}$$

$$K = \exp\left(-\frac{\Delta G°}{RT} \right) = \exp\left(\frac{16.37 \cdot 10^3 J \cdot mol \cdot K}{mol \cdot 8.314 J \cdot 298.15 K} \right) = 738$$

Calculate X from K:
$$d\xi = \frac{1}{\nu_i} dn_i \Rightarrow \int_{n_{i0}}^{n_i} dn_i = \nu_i \int_0^\xi d\xi \Rightarrow n_i = n_{i0} + \nu_i \xi$$

Species	ν_i	n_{i0}/mol	n_i/mol	x_i
N_2	-1/2	1/2	1/2-1/2ξ	(1/2-1/2ξ)/(2-ξ)
H_2	-3/2	3/2	3/2-3/2ξ	(3/2-3/2ξ)/(2-ξ)
NH_3	1	0	ξ	ξ/(2-ξ)
Σ		2	2-ξ	1

$$X = \frac{n_{N2,0} - n_{N2}}{n_{N2,0}}$$

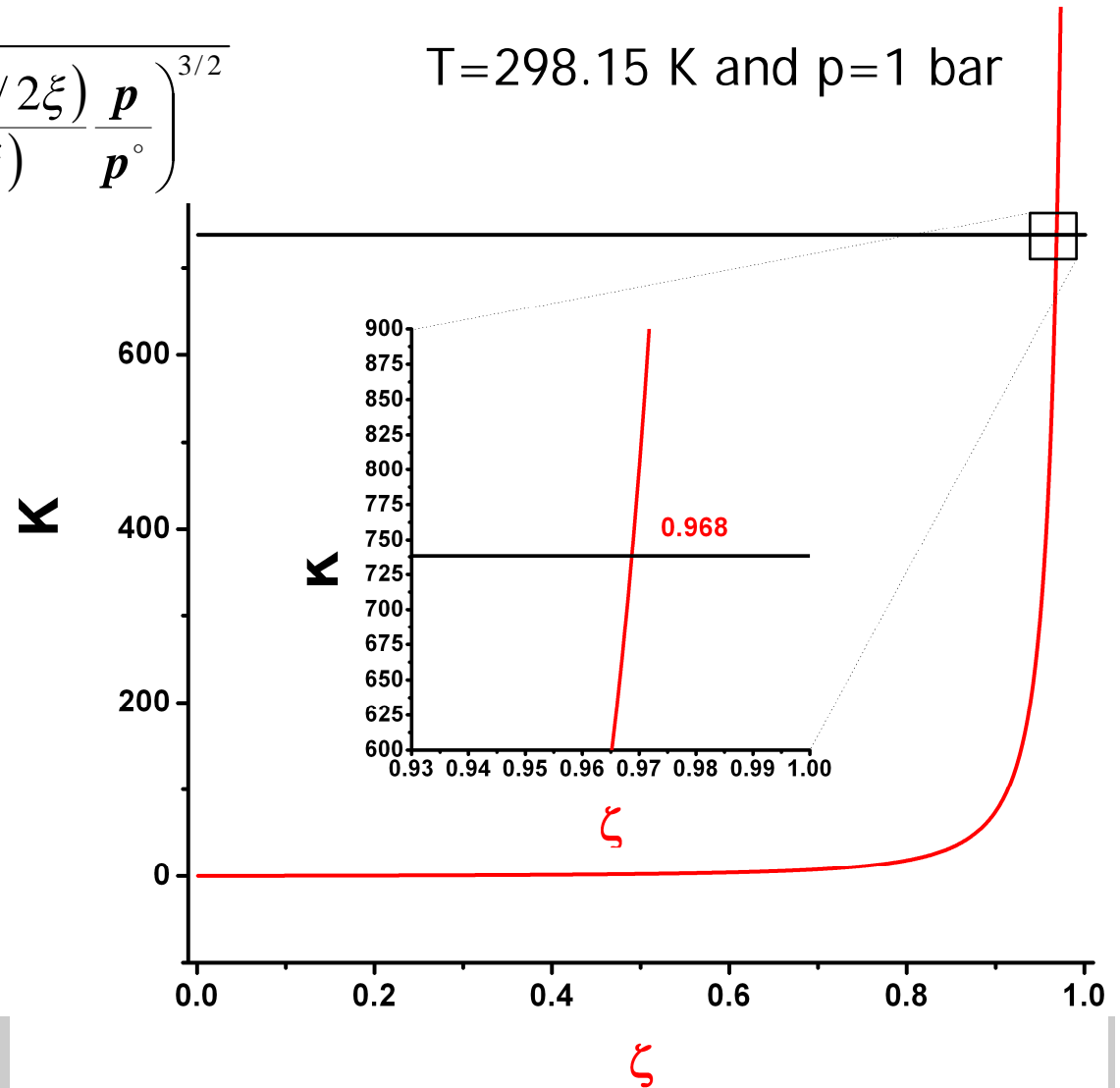$$= \frac{-\nu_{N2}\xi}{n_{N2,0}} = \frac{-(-1/2)\xi}{1/2} = \xi$$

$$K = \prod_i a_i^{\nu_i} = \frac{\left(\dfrac{p_{NH3}}{p^\circ}\right)^1}{\left(\dfrac{p_{N2}}{p^\circ}\right)^{1/2}\left(\dfrac{p_{H2}}{p^\circ}\right)^{3/2}} = \frac{\left(\dfrac{\xi}{(2-\xi)}\dfrac{p}{p^\circ}\right)^1}{\left(\dfrac{(1/2-1/2\xi)}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{1/2}\left(\dfrac{(3/2-3/2\xi)}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{3/2}}$$

$$738 = \frac{\left(\dfrac{\xi}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{1}}{\left(\dfrac{(1/2-1/2\xi)}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{1/2}\left(\dfrac{(3/2-3/2\xi)}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{3/2}}$$

T=298.15 K and p=1 bar

Solution: Graphical Solution
(e.g. with Excel, Origin....)

0.968

T dependance of K:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \Rightarrow \ln K(T) = \ln K(T_1) + \int_{T_1}^{T} \frac{\Delta H^\circ(T')}{RT'^2} dT'$$

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) + \int_{T_1}^{T} \Delta C_p^\circ(T') dT'$$

Species ν_i		ΔH_f° / kJ·mol^{-1}	S° / J·mol^{-1}·K^{-1}	C_p° / J·mol^{-1}·K^{-1}		
				A	B	C
N$_2$	-1/2	0	191.6	24.98	5.912	-0.3376
H$_2$	-3/2	0	130.7	29.07	-0.8368	2.012
NH$_3$	1	-45.9	192.8	25.93	32.58	-3.046

$$\Delta C_p^0(T) = \Delta A + \Delta B \cdot T + \Delta C \cdot T^2 \quad \Delta A = \sum_i \nu_i A_i ....$$

$$\Delta C_p^0(T) = -30.17 + 30.9 \cdot 10^{-3} \cdot T - 5.90 \cdot 10^{-6} \cdot T^2$$

T dependance of K:

$$\Delta H^{\circ}(T) = \Delta H^{\circ}(T_1) + \int_{T_1}^{T} \Delta C_p^{\circ}(T') dT'$$

$$\Delta C_p^{0}(T) = \Delta A + \Delta B \cdot T + \Delta C \cdot T^2$$

$$\Delta H^{\circ}(T) = \Delta H^{\circ}(T_1) + \int_{T_1}^{T} \left(\Delta A + \Delta B \cdot T' + \Delta C \cdot T'^2\right) dT'$$

$$= \Delta H^{\circ}(T_1) + \Delta A(T - T_1) + \frac{\Delta B}{2}\left(T^2 - T_1^2\right) + \frac{\Delta C}{3}\left(T^3 - T_1^3\right)$$

$$= \Delta H^{\circ}(T_1) - \Delta A \cdot T_1 - \frac{\Delta B}{2} T_1^2 - \frac{\Delta C}{3} T_1^3 + \Delta A \cdot T + \frac{\Delta B}{2} T^2 + \frac{\Delta C}{3} T^3$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^{\circ}}{RT^2} \Rightarrow \ln K(T) = \ln K(T_1) + \int_{T_1}^{T} \frac{\Delta H^{\circ}(T')}{RT'^2} dT'$$

T dependance of K:

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) - \Delta A \cdot T_1 - \frac{\Delta B}{2}T_1^2 - \frac{\Delta C}{3}T_1^3 + \Delta A \cdot T + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{3}T^3$$

$$\frac{\Delta H^\circ(T)}{RT^2} = \frac{const.}{RT^2} + \frac{\Delta A}{RT} + \frac{\Delta B}{2R} + \frac{\Delta C}{3R}T$$

$$const. = \Delta H^\circ(T_1) - \Delta A \cdot T_1 - \frac{\Delta B}{2}T_1^2 - \frac{\Delta C}{3}T_1^3$$

$$\ln K(T) = \ln K(T_1) + \int_{T_1}^{T}\left[\frac{const.}{RT'^2} + \frac{\Delta A}{RT} + \frac{\Delta B}{2R} + \frac{\Delta C}{3R}T'\right]dT'$$

$$\ln K(T) = \ln K(T_1) + \frac{const.}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right] + \frac{\Delta A}{R}\ln\frac{T}{T_1} + \frac{\Delta B}{2R}(T - T_1) + \frac{\Delta C}{6R}\left[T^2 - T_1^2\right]$$

T dependance of K:

$$\ln K(T) = \ln K(T_1) + \frac{const.}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right] + \frac{\Delta A}{R}\ln\frac{T}{T_1} + \frac{\Delta B}{2R}(T - T_1) + \frac{\Delta C}{6R}\left[T^2 - T_1^2\right]$$
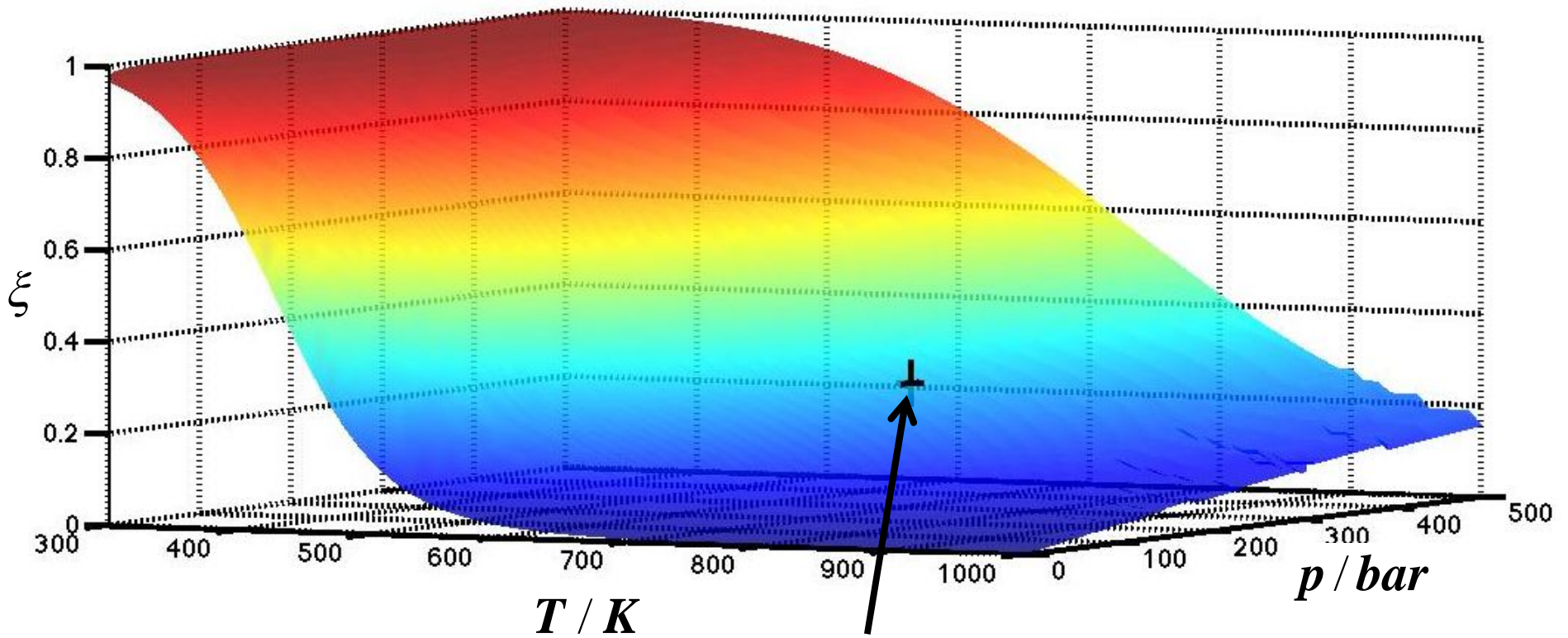
Solve

$$\exp(\ln K(T)) = \frac{\left(\dfrac{\xi}{(2-\xi)}\dfrac{p}{p^\circ}\right)^1}{\left(\dfrac{(1/2-1/2\xi)}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{1/2}\left(\dfrac{(3/2-3/2\xi)}{(2-\xi)}\dfrac{p}{p^\circ}\right)^{3/2}}$$

numerically or graphically with p and T as parameters gives $\xi = \xi(p,T)$!

Solution: Numerical Solution (e.g. with Matlab, Mathematica....)

typical process conditions for industrial ammonia synthesis

Thermodynamics says nothing about the rate at which a process proceeds!

$$SO_2 + 1/2O_2 \xrightarrow{\quad V_2O_5, K_2SO_4 (400-600°C) \quad} SO_3$$
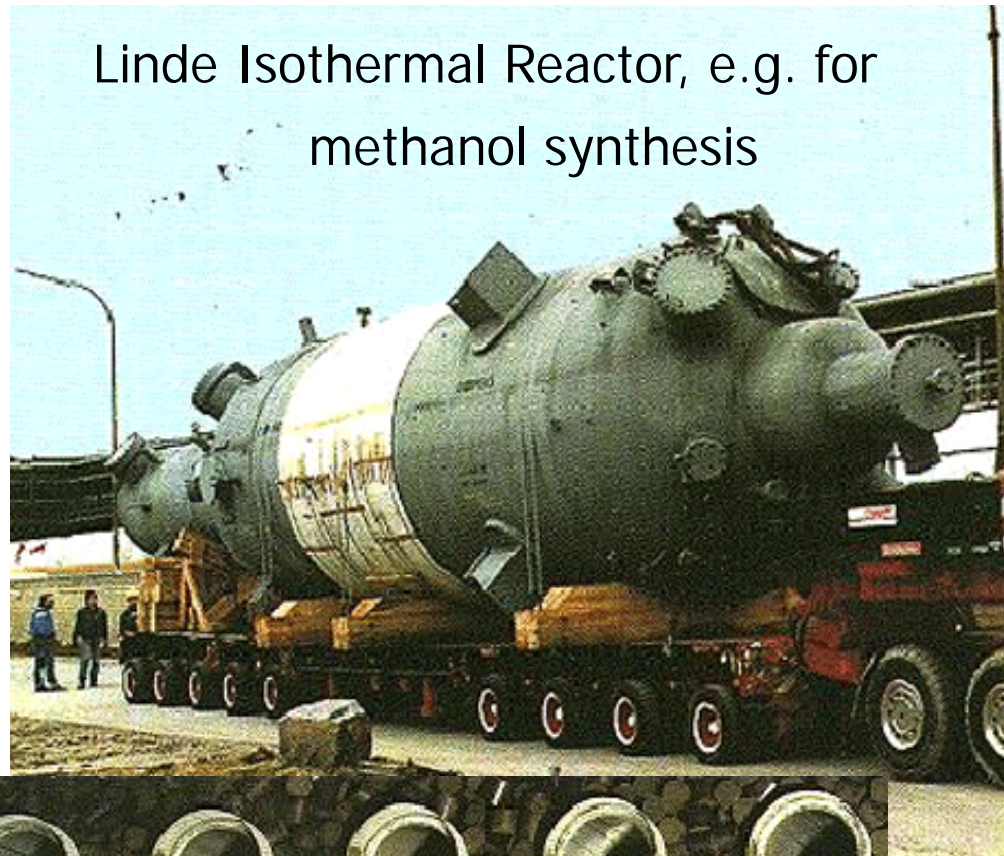
$$\Delta_r H = -99 kJ / mol$$
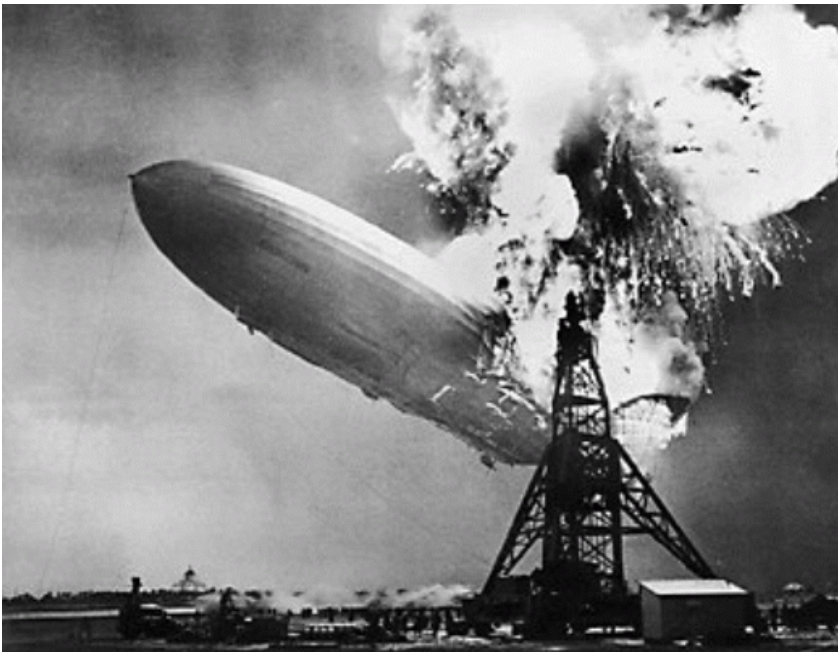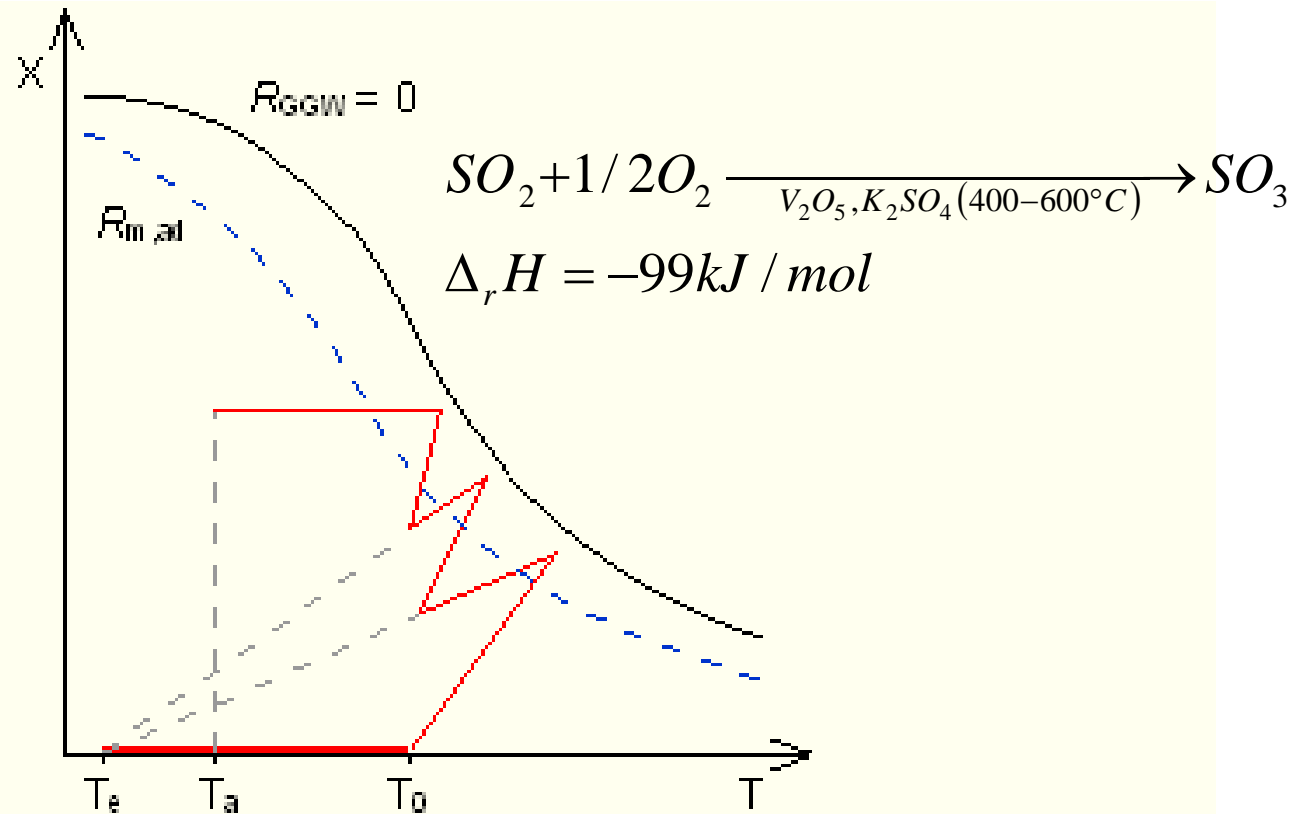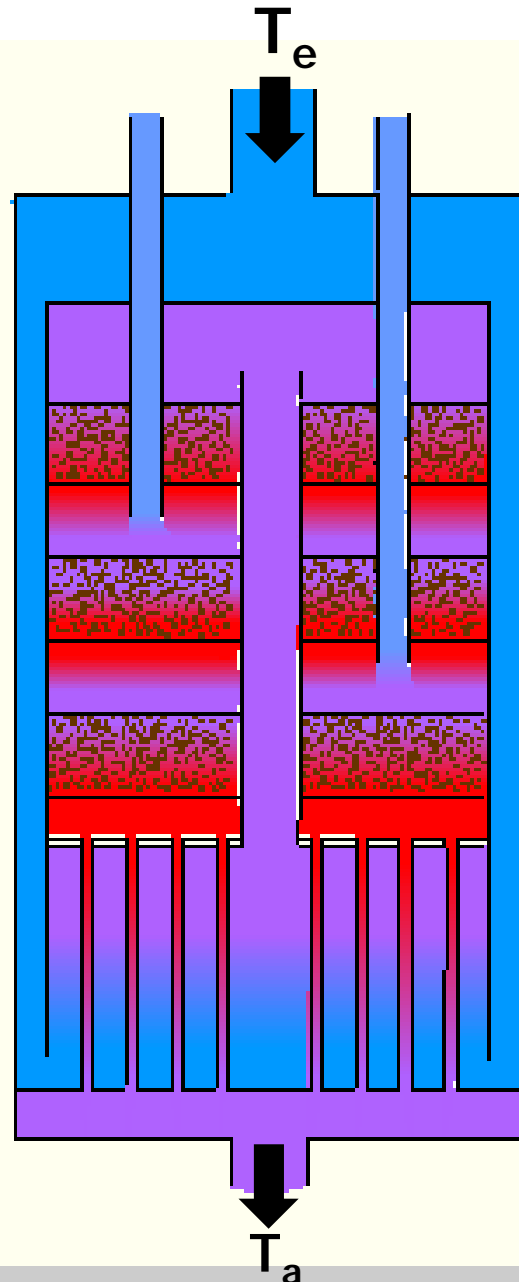
X	- Umsatz
T	- Temperatur
T_0	- Hordeneintrittstemperatur
T_e	- Kaltgaseintrittstemperatur
T_a	- Austrittstemperatur des Reaktionsgemisches
R_{GGW}	- Reaktionsgeschwindigkeit im Gleichgewichtszustand
$R_{m,ad}$	- maximale adiabate Reaktionsgeschwindigkeit

45

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta_r H(300K) = -90.8\, kJ/mol$$

Steam

Circulating water

Boiler feed water

Gas entry

Circulating water

Gas exit

Linde Isothermal Reactor, e.g. for methanol synthesis

4.1 Theory

$$(G)_{T,p} = G(n_1, n_2, ..., n_N) = \min$$

but the n_i cannot vary independently because they have to fulfill the materials balances

moles of species i in the reaction mixture

$$\sum_{i=1}^{N} a_{ki} n_i = b_k \leftarrow$$

total moles of atoms of element k in the reaction mixtures

number of atoms of element k in species i

$$\sum_{i=1}^{N} a_{ki} n_i - b_k = 0 \quad \lambda_k \left(\sum_{i=1}^{N} a_{ki} n_i - b_k \right) = 0 \quad \sum_{k=1}^{M} \lambda_k \left(\sum_{i=1}^{N} a_{ki} n_i - b_k \right) = 0$$

Lagrange Multipliers

4.1 Theory

$$F = (G)_{T,p} + \sum_{k=1}^{M} \lambda_k \left(\sum_{i=1}^{N} a_{ki} n_i - b_k \right)$$

↑

Lagrange Function

$$\left(\frac{\partial F}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} + \sum_{k=1}^{M} \lambda_k a_{ki} = \mu_i + \sum_{k=1}^{M} \lambda_k a_{ki} = 0$$

$$G_i^0 + RT \ln a_i + \sum_{k=1}^{M} \lambda_k a_{ki} = 0$$

set of N equations
(1 for each of the N species)

$$\lambda_k \left(\sum_{i=1}^{N} a_{ki} n_i - b_k \right) = 0$$

set of M equations
(1 for each of the M elements)

N + M unknowns (n - mole numbers + m - lambdas)

4.2 Example: Calculate the equilibrium composition of a steam reforming mixture consisting of CH_4, H_2O, CO, CO_2 and H_2 at T=1000K and p=1bar. $n_{0,CH4}=2$mol, $n_{0,H2O}=3$mol. Ideal gases can be assumed.

From thermodynamic tables (e.g. CRC Handbook) we extract:

Species	CH_4	H_2O	CO	CO_2	H_2
$\Delta G_f°$ (1000K) / $J \cdot mol^{-1}$	19475	-192603	-200281	-395865	0

From the species formulas we obtain:

Species	CH_4	H_2O	CO	CO_2	H_2
# of C atoms	$a_{C,CH4}=1$	$a_{C,H2O}=0$	$a_{C,CO}=1$	$a_{C,CO2}=1$	$a_{C,H2}=0$
# of O atoms	$a_{O,CH4}=0$	$a_{O,H2O}=1$	$a_{O,CO}=1$	$a_{O,CO2}=2$	$a_{O,H2}=0$
# of H atoms	$a_{H,CH4}=4$	$a_{H,H2O}=2$	$a_{H,CO}=0$	$a_{H,CO2}=0$	$a_{H,H2}=2$

4.2 Example: Formulating the equations

$$\frac{\Delta G^0_{f,i}}{RT} + \ln a_i + \sum_{k=1}^{M} \frac{\lambda_k}{RT} a_{ki} = 0 \quad \bigg| \quad a_i = \frac{p_i}{p^\circ} = x_i \frac{p}{p^\circ} = \frac{n_i}{\sum_i n_i} \frac{1bar}{1bar} = \frac{n_i}{\sum_i n_i}$$

CH_4:
$$\frac{19475}{8.314 \cdot 1000} + \ln\left(\frac{n_{CH4}}{\sum_i n_i}\right) + \frac{\lambda_C}{8.314 \cdot 1000} + \frac{4\lambda_H}{8.314 \cdot 1000} = 0$$

H_2O:
$$\frac{-192603}{8.314 \cdot 1000} + \ln\left(\frac{n_{H2O}}{\sum_i n_i}\right) + \frac{2\lambda_H}{8.314 \cdot 1000} + \frac{\lambda_O}{8.314 \cdot 1000} = 0$$

CO:
$$\frac{-200281}{8.314 \cdot 1000} + \ln\left(\frac{n_{CO}}{\sum_i n_i}\right) + \frac{\lambda_C}{8.314 \cdot 1000} + \frac{\lambda_O}{8.314 \cdot 1000} = 0$$

CO_2:
$$\frac{-395865}{8.314 \cdot 1000} + \ln\left(\frac{n_{CO2}}{\sum_i n_i}\right) + \frac{\lambda_C}{8.314 \cdot 1000} + \frac{2\lambda_O}{8.314 \cdot 1000} = 0$$

H_2:
$$\ln\left(\frac{n_{H2}}{\sum_i n_i}\right) + \frac{2\lambda_H}{8.314 \cdot 1000} = 0$$

starting values

$n_{0,CH4} = 2$ mol

$n_{0,H2O} = 3$ mol.

atom balance on C
$$n_{CH4} + n_{CO} + n_{CO2} - 2 = 0$$

atom balance on O
$$n_{H2O} + n_{CO} + 2n_{CO2} - 3 = 0$$

atom balance on H
$$4n_{CH4} + 2n_{H2O} + 2n_{H2} - 14 = 0$$

4.2 Example: Solving the system of nonlinear equations e.g in Matlab (fsolve)

$$n_{CH4} = 0.175$$

$$n_{H2O} = 0.856$$

$$n_{CO} = 1.507$$

$$n_{CO2} = 0.319$$

$$n_{H2} = 5.795$$

$$\sum_i n_i = 8.651$$

$$x_{CH4} = 0.0202$$

$$x_{H2O} = 0.0990$$

$$x_{CO} = 0.1742$$

$$x_{CO2} = 0.0368$$

$$x_{H2} = 0.6698$$

$$\sum_i x_i = 1$$

The most difficult thing is to find starting values that work. Make educated guesses based on physical or chemical knowledge ($0 \leq x_i \leq 1$), e.g.

$$\ln\left(\frac{n_{H2}}{\sum_i n_i}\right) + \frac{2\lambda_H}{8.314 \cdot 1000} = 0 \Rightarrow \lambda_{H,0} = \frac{-8.314 \cdot 1000 \cdot \ln 0.5}{2} = 2881$$

4.3 Another Example: Equilibrium Calculations with CHEMKIN

Methan Oxidation on Rh and Pt Coated Foam Catalysts
(T ≈ 1000°C)
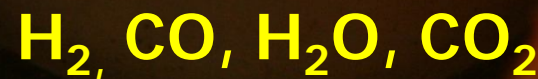
$CH_4 + O_2$

$\tau \sim 10^{-3}$ s

p, H const.
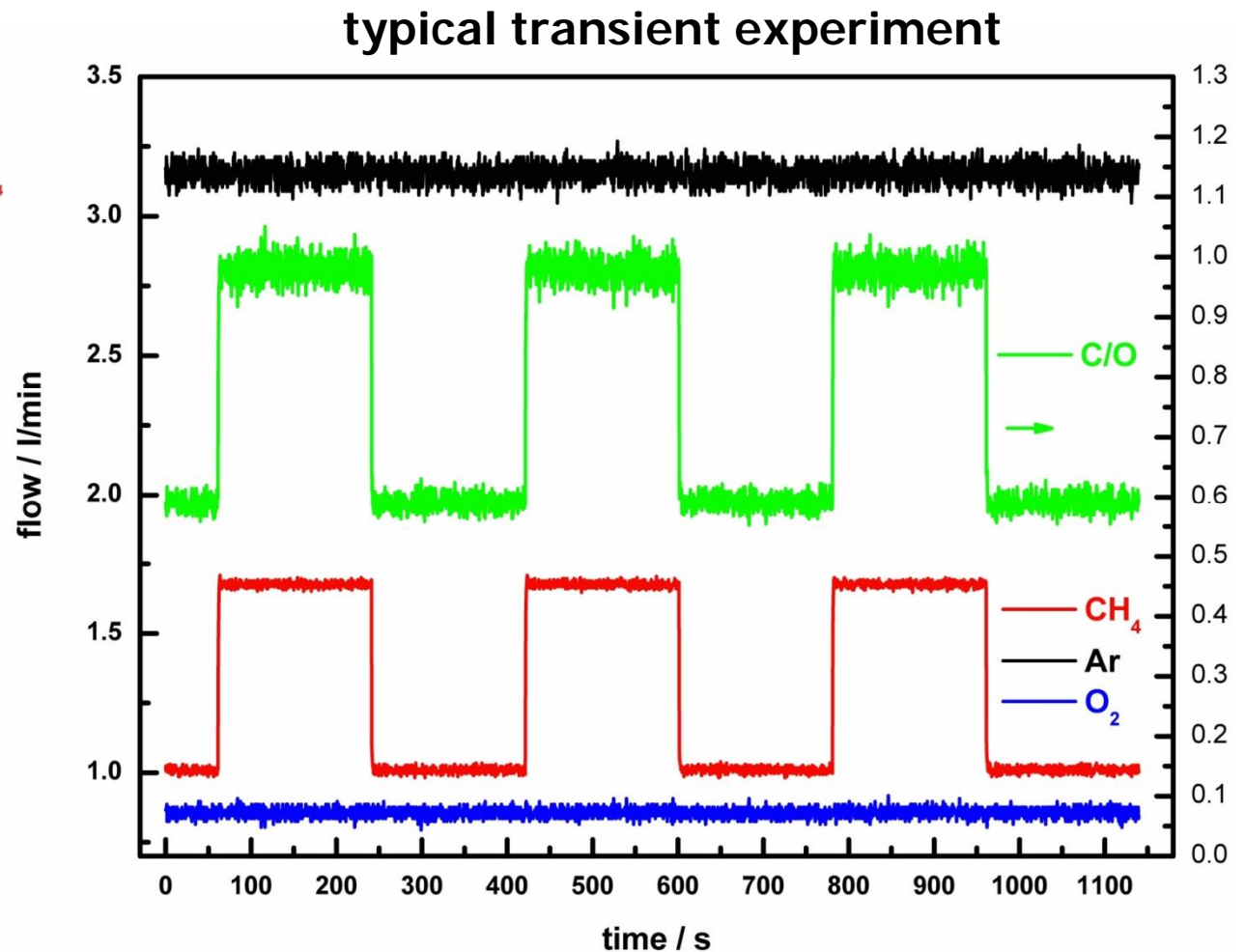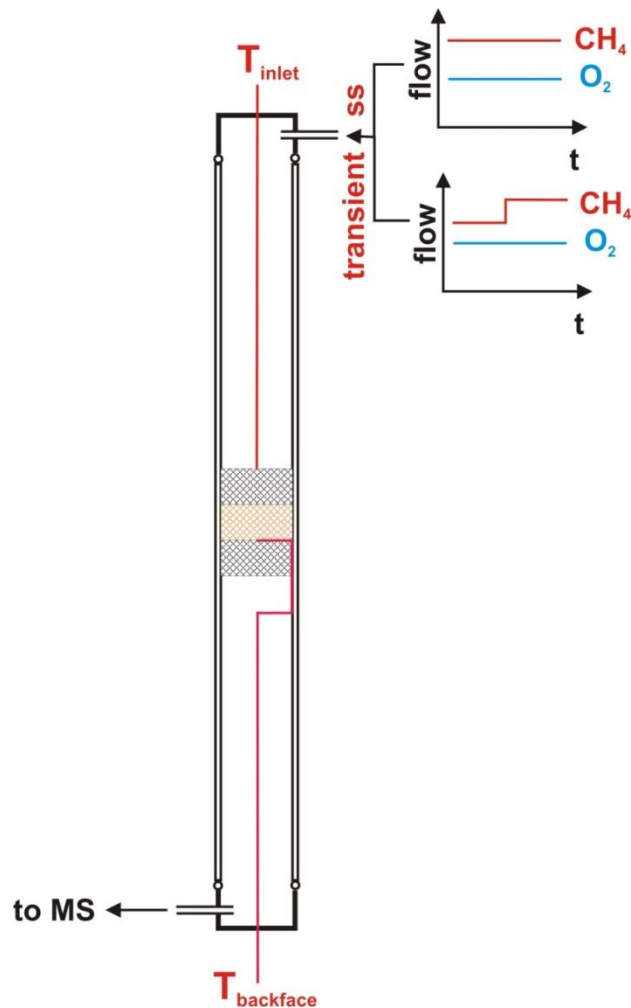
H_2, CO, H_2O, CO_2

4.3 Another Example: Equilibrium Calculations with CHEMKIN

5 wt% Rh on 80ppi α-Al$_2$O$_3$ foam, feed 5 ln/min, C/O = 1.0, Ar/O$_2$ = 79/21, 1 bar
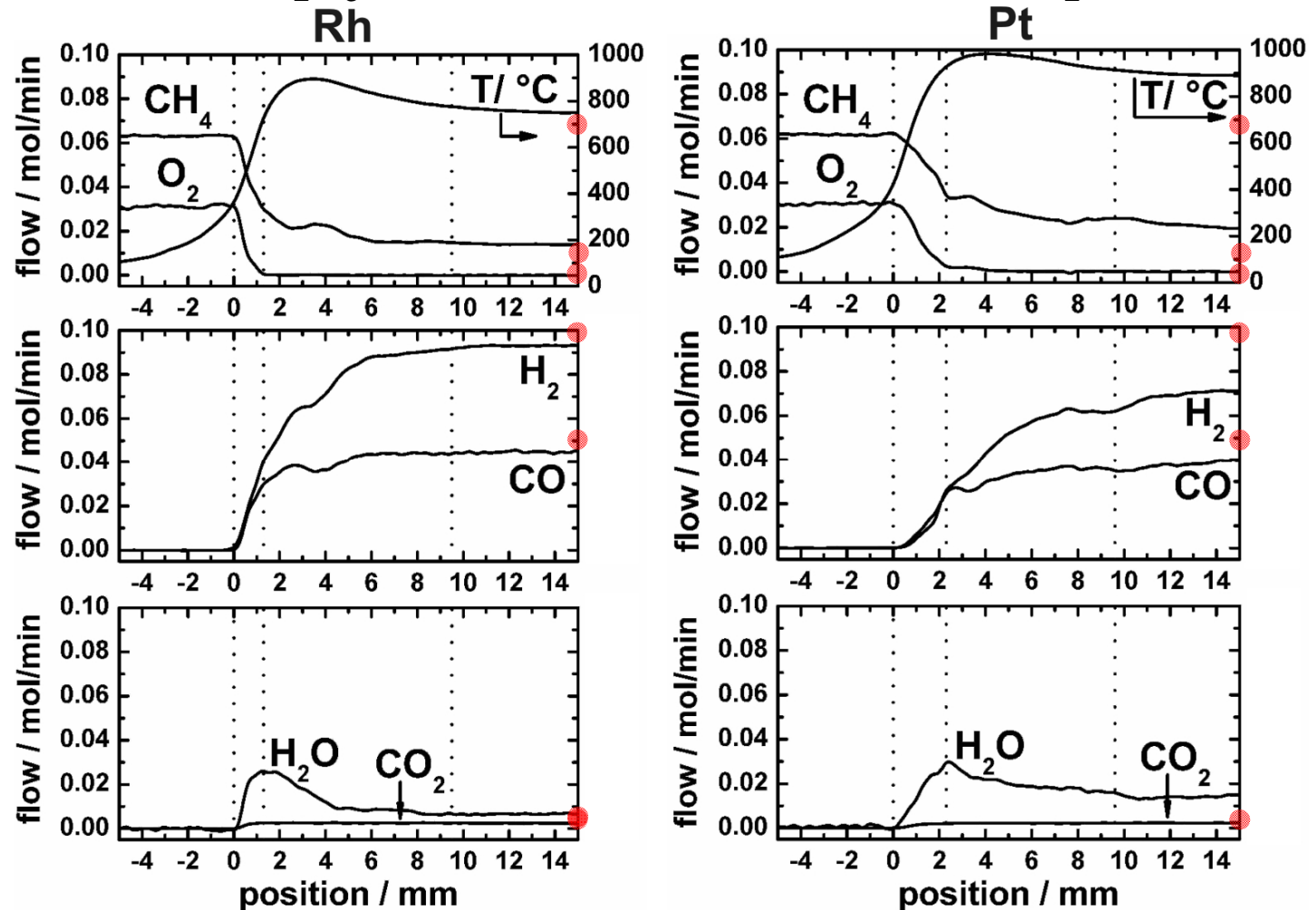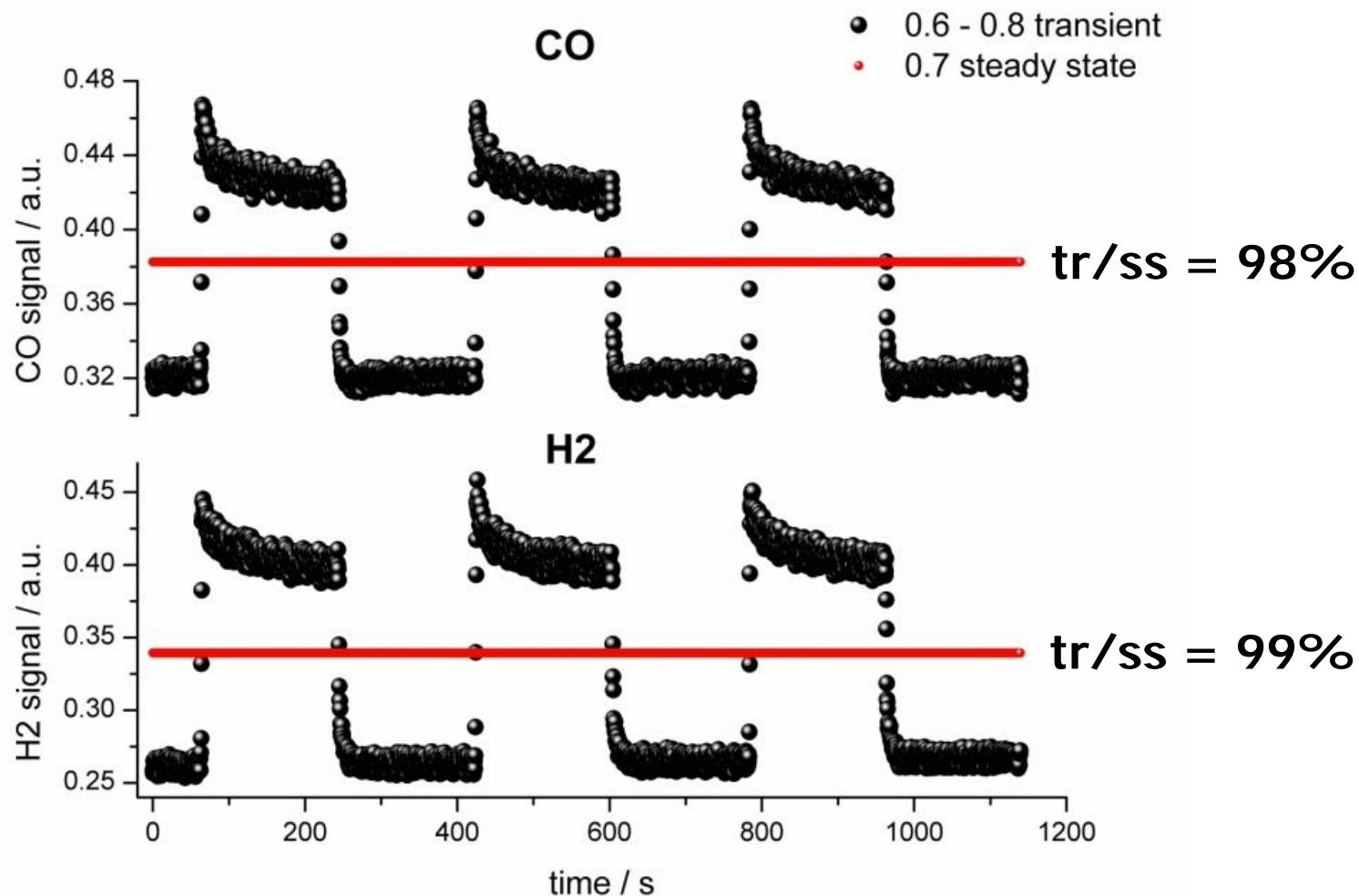
4.4 Take home message: Some months in the Lab can save you one day in the Library!!!

typical transient experiment

4.4 Take home message: Some months in the Lab can save you one day in the Library!!!

tr/ss = 98%

tr/ss = 99%

Kinetics

$$-r_A = k(T)C_A(T)$$

T

Equilibrium

$$\ln K = -\frac{\Delta_R G^0}{RT}$$

$$[A^*] = \frac{K_{ads}[A][*]_0}{1 + K_{ads}[A]}$$

Transport

$$\vec{J}_A = -D_{AB}(T)\nabla C_A(T)$$

$$v = v_0 \frac{F_T}{F_{T0}} \frac{p_0}{p} \frac{T}{T_0}$$
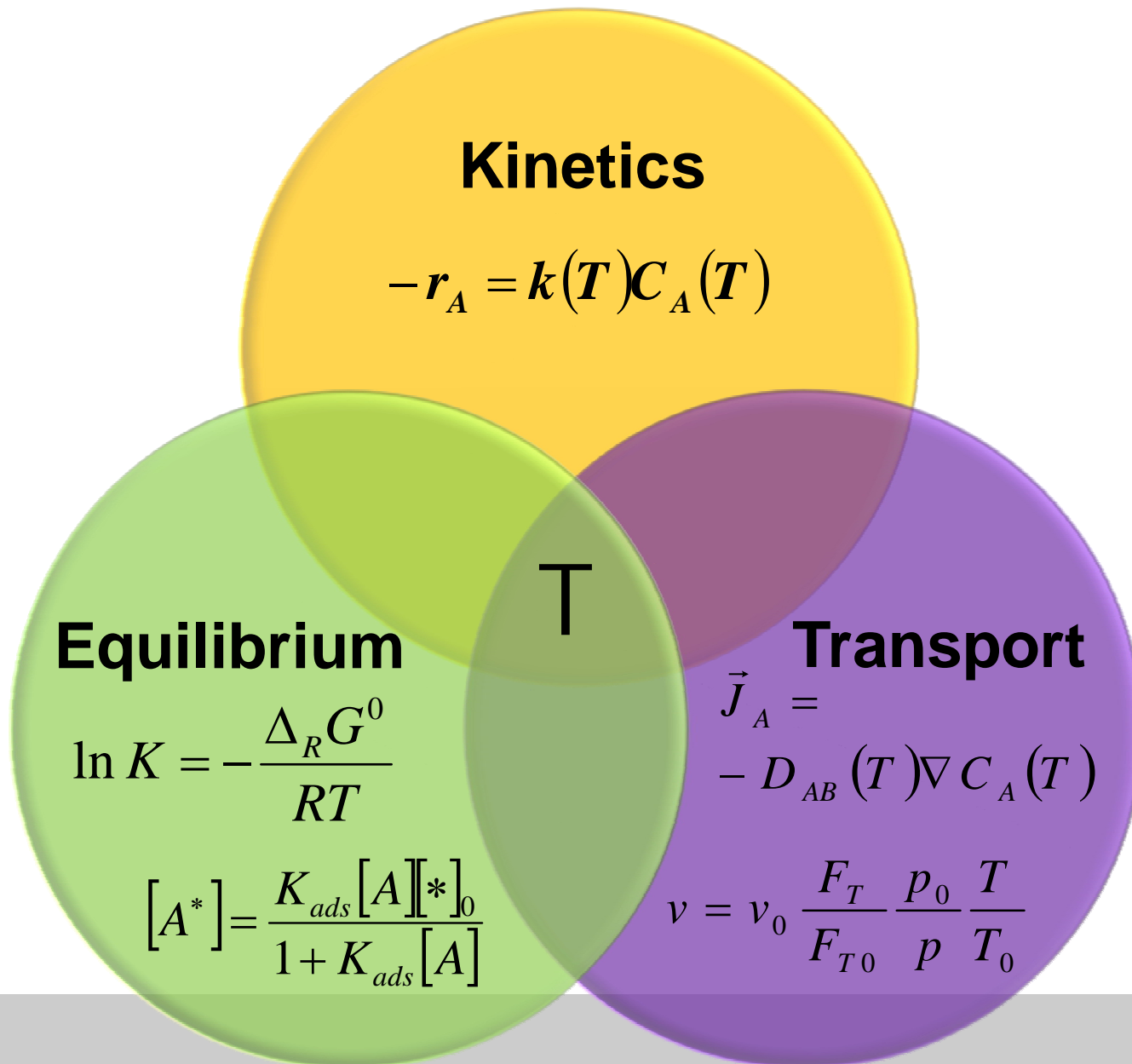
Maybe the better way to deal with Thermodynamics?
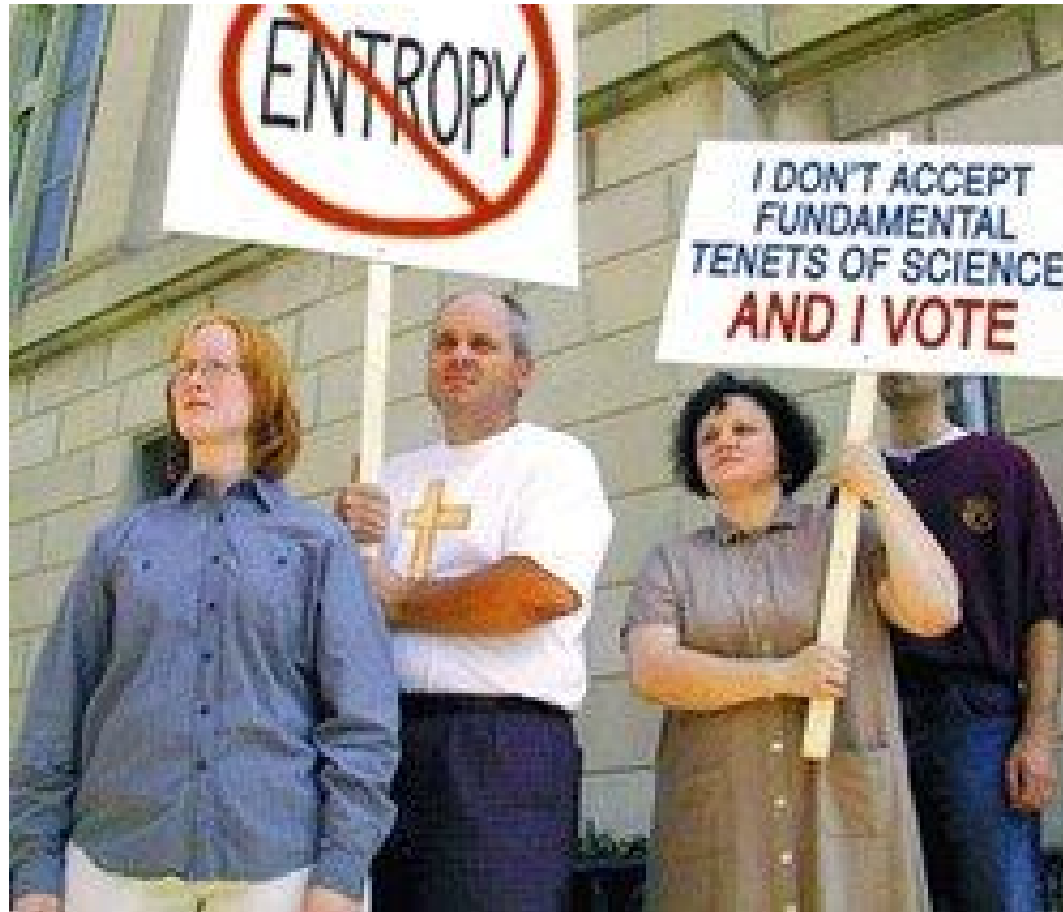
Thank you very much for your attention!!!