# The Entropy-free Thermodynamics of Processes (ETIP) and Classical TIP as One of Its Special Cases

1. Structure of Thermodynamic Theories
2. Entropy and the 2nd Law of Thermodynamics
3. Does there exist a Non-Equilibrium Entropy?
4. The formalism of ETIP
5. Examples:
   Stationary adiabatic gas flow
   Mixture gas adsorption
   Protein denaturation upon adsorption

## Thermodynamic Theories of Processes

1. Classical TIP
2. Generalized / Extended TIP
3. Nonlinear Field Theories / Rational Thermodynamics
4. Variational Formalism
5. Entropy-free Thermodynamics of Processes

## Physical Structure

A. Thermostatics

B. Balance Equations / Conservation Laws ($1^{st}$ Law)

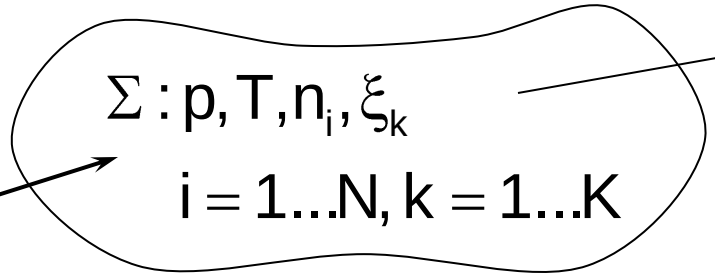
C. Process / Constitutive Equations ($2^{nd}$ Law)

D. Initial- & Boundary Conditions

# Thermodynamic System (W. Schottky, 1929)

Exchange processes ($\Sigma \leftrightarrow \Sigma^*$): heat, work, mass, …

$$\dot{n}^{(\alpha)} = \sum_{i=1}^{N} \dot{n}_i^{(\alpha)}$$




Internal variables
Bridgeman, Meixner,
Kestin, Flory

$$\dot{Q}, \dot{W} = -p^* \dot{V}$$

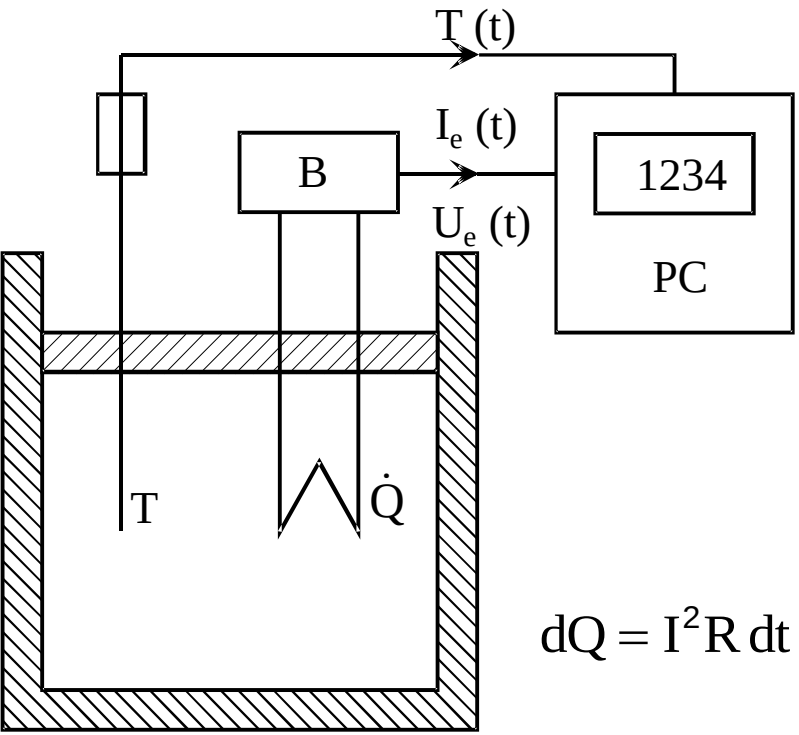
$$\Sigma^* : p^*, T^*, h^{(\alpha)}, s^{(\alpha)}, \mu_i^{(\alpha)}$$

$$\alpha = 1...A$$

Simple System: No external forces
surface phenomena
radiation effects

# 2nd Law (1): Clausius Entropy

$$S\ Z = S\ Z_0 + \oint_{Z_0}^{Z} \frac{dQ_{rev}}{T} \quad \ldots \quad dT \to 0$$




Entropymeter

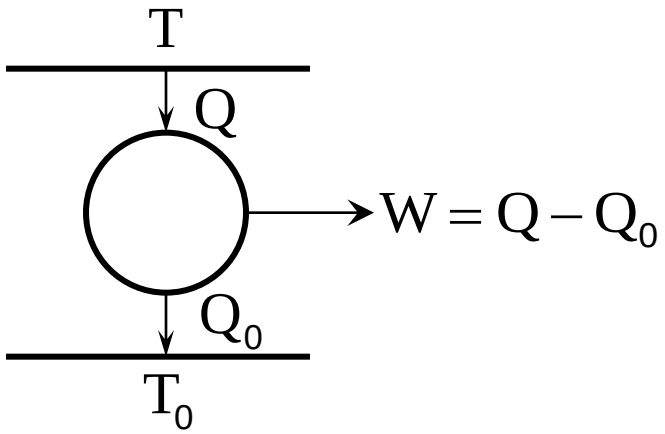
Clausius Equality $Z = Z_0$

$$0 = \oint \frac{dQ_{rev}}{T}$$

Carnot-Relation

$$\frac{Q}{T} = \frac{Q_0}{T_0} \quad , \quad \eta_c = \frac{W}{Q} = 1 - \frac{T_0}{T}$$

$$dQ = I^2 R\, dt$$

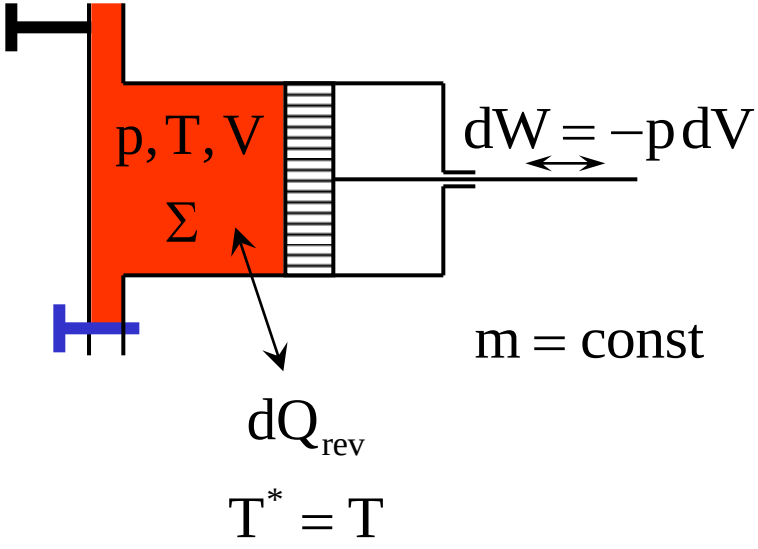


# Gibbs Equation (Simple System)

1st Law : $dU = dQ_{rev} - p\,dV$

2nd Law: $dS = dQ_{rev}/T$

Gibbs: $dS = \frac{1}{T}dU + \frac{p}{T}dV$

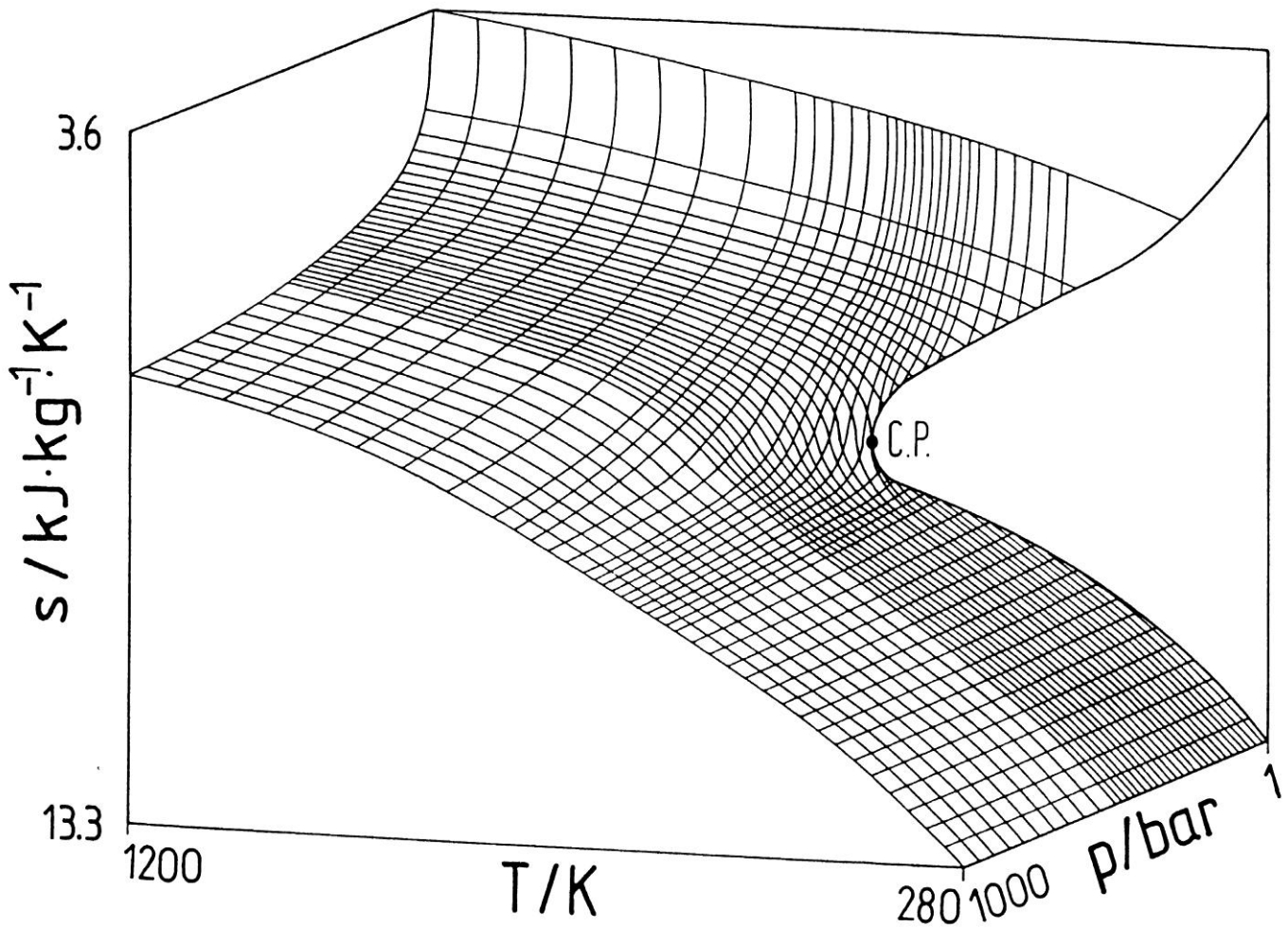



$$\left(\frac{\partial^2 S}{\partial T\,\partial V}\right) = \left(\frac{\partial^2 S}{\partial V\,\partial T}\right) \rightarrow S = S_0 + \int_{T_0(V_0)}^{T} \frac{C_{V_0}}{T'}\,dT' + \int_{V_0(T)}^{V} \left[\frac{\partial p\ T, V'}{\partial T}\right]_T dV'$$

Caloric EOS  Thermal EOS

# Entropy of Water ($H_2O$)

K. Stephan, W. Wagner
IAPS (1985)



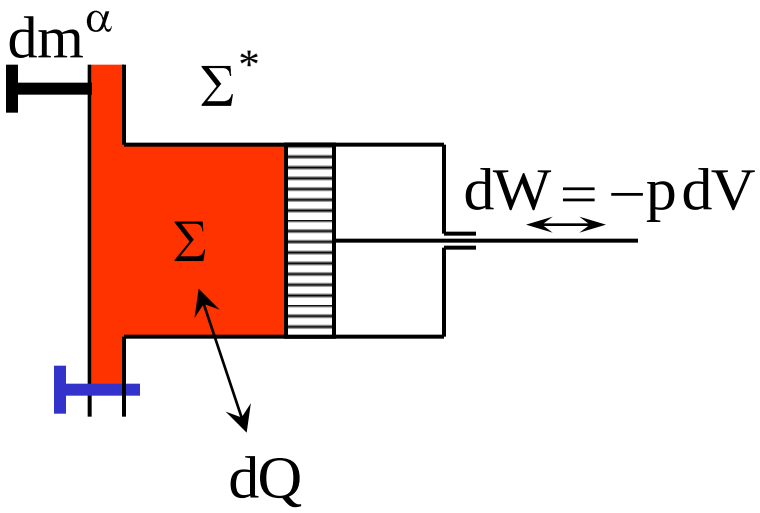
# Interpretations of the Clausius Entropy (S(Z))

1. M. Planck (1885)
   Measure for “probability”, tendency, preference of a system to actually realize a certain equilibrium state (Z).
   ($N_2$-gas in steel bottle)

2. L. Boltzmann (1890)
   Measure for molecular “disorder” in a system in state (Z).
   (Crystal, liquid, gas, plasma ...)

3. C. Shannon (1948)
   Measure for “lack of knowledge” of the micro- i.e. molecular state of a system ($\Sigma$) in a given macroscopic state (Z)

# 2nd Law (2): Clausius Inequality




Exchange of
mass heat work

$$\Sigma: \quad Z_0 \rightarrow Z$$

IRR :
REV :

$$S - S_0 \geq \oint_{Z_0}^{Z} \left( \frac{dQ}{T^*} + \sum_{\alpha} s^{\alpha}\, dm^{\alpha} \right)$$

Quasistatic changes of state ($Z \rightarrow Z + dZ$)

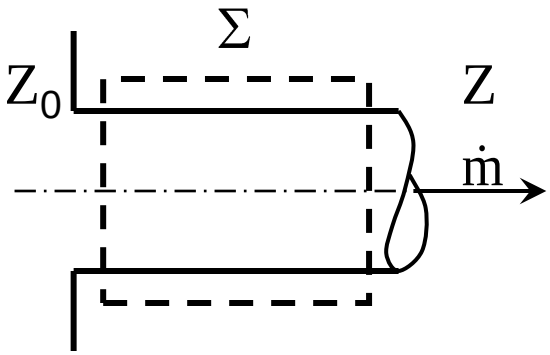
$$dS \geq \frac{dQ}{T^*} + \sum_{\alpha=1}^{A} s^{(\alpha)} dn^{(\alpha)}$$

Closed Systems: $dQ = 0\,, \; dm^{\alpha} = 0$

IRR :
REV :

$S \geq S$ ... World Statement?

# Example 1: Stationary Adiabatic Ideal Gas Flow




MB : $\dot{m} = A_0 w_0 \rho_0 = A\, w\, \rho = \text{const} = ?$ 1

ENB : $h_0 + \frac{1}{2} w_0^2 = h + \frac{1}{2} w^2$ 2

TEOS: $\rho = p / R\,T \quad , \quad R = \mathbb{R}/M$ 3

CEOS: $h = h_0 + c_p\ T - T_0$ 4

$$c_p = \frac{\kappa}{\kappa - 1} R$$

$Z_0$ : $p_0, T_0, \rho_0, A_0 \to \infty, w_0 \to 0$

$Z$ : $\underline{p}, T, \rho, \underline{A}, w$

1–4 : $\frac{1}{2} w^2 = c_p\ T_0 - T$ 5

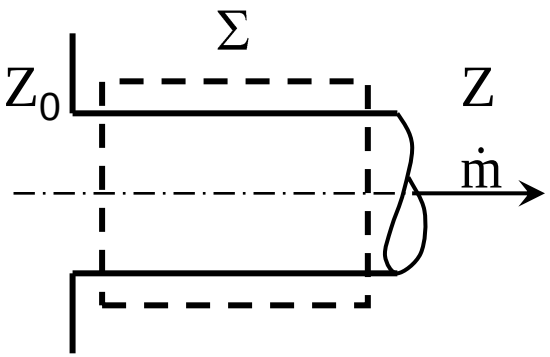
W : $\dot{m}, T, w$ G : $Z_0, p, A$

RFA : 5, 6, 1

Rev. flow approximation (RFA)

$$p_0 T_0^{\omega} = p\, T^{\omega} \quad , \quad \omega = \frac{\kappa}{1 - \kappa}$$ 6

# Example 1: Stationary Adiabatic Ideal Gas Flow




$Z_0$ : $p_0, T_0, \rho_0, A_0 \to \infty, w_0 \to 0$

$Z$ : $p, T, \rho, A, w$

2nd Law (2), Clausius Inequality

$$0 \geq s_0 - s \quad \dot{m} \qquad 7$$

Eckart-Onsager-Principle

$$\dot{m} = L \quad s - s_0 \quad , \quad L \geq 0 \qquad 8$$

Ideal gas entropy

$$s - s_0 = c_p \ln\left(\frac{T}{T_0}\right) - R \ln\left(\frac{p}{p_0}\right) \qquad 9$$

$$8,9 \quad T = T_0 \left( \frac{p}{p_0} e^{\frac{\dot{m}}{L R}} \right)^{1/\omega} \quad , \quad \omega = \frac{\kappa}{1-\kappa} \qquad 10$$

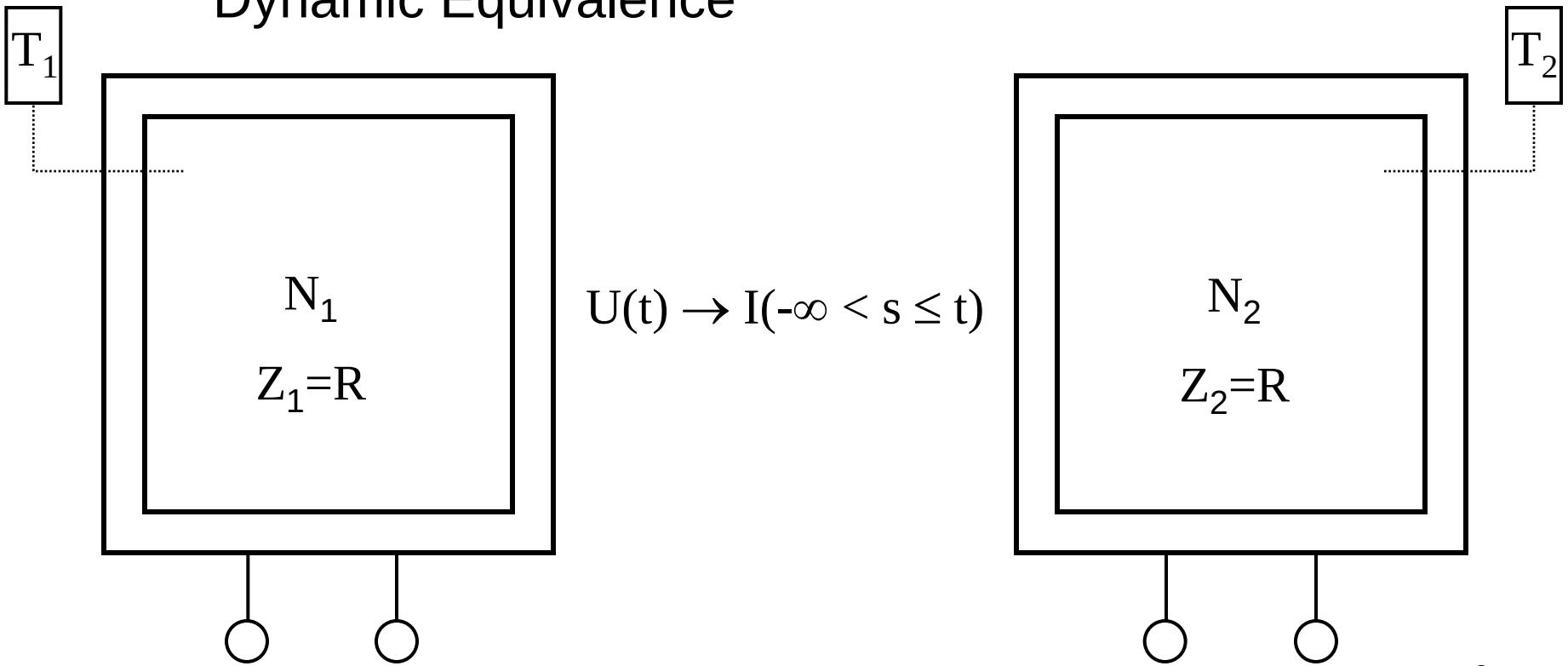
Adiabatic equation for irrev. ideal gas flow

Limiting case: $L \to \infty, s \to s_0$, 10 $\to$ 6

Reversible flow

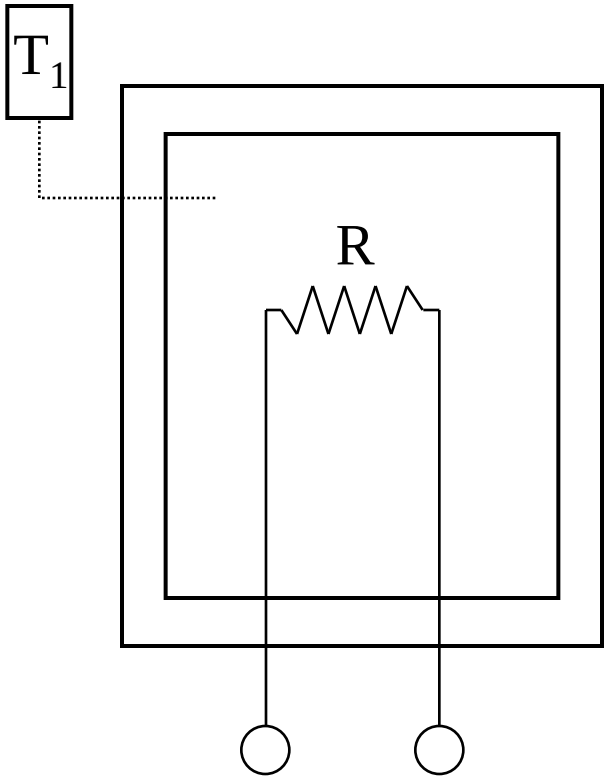
# 3. Non-Uniqueness of "Non-Equilibrium Entropy"

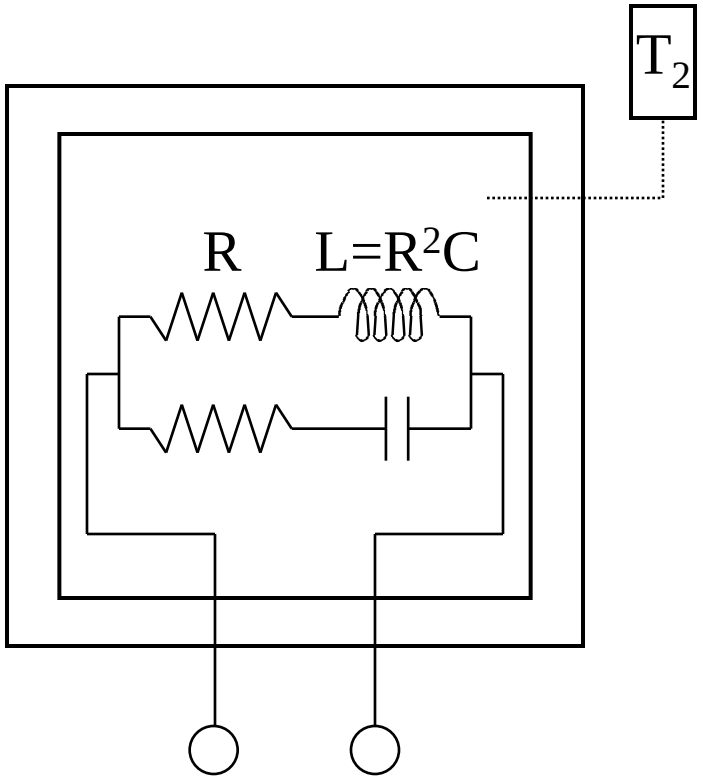
Adiabatic Electrical Networks ($N_1$, $N_2$)
Identical Impedance Functions ($Z_1=Z_2=R$)
Dynamic Equivalence




$$N_1: I_1(t) = \frac{U_1(t)}{R} \;,\; \dot{S}_1 = \frac{I_1 U_1}{T_1} = \frac{U_1^2}{T_1 R} \qquad N_2: I_2(t) = \frac{U_2(t)}{R} \;,\; \dot{S}_2 = \frac{I_2 U_2}{T_2} = \frac{U_2^2}{T_2 R} \quad ?$$

# Adiabatic Electrical Networks ($N_1$, $N_2$)
# Identical Impedance Functions ($Z_1$=$Z_2$=R)




$$Z_1 = R$$

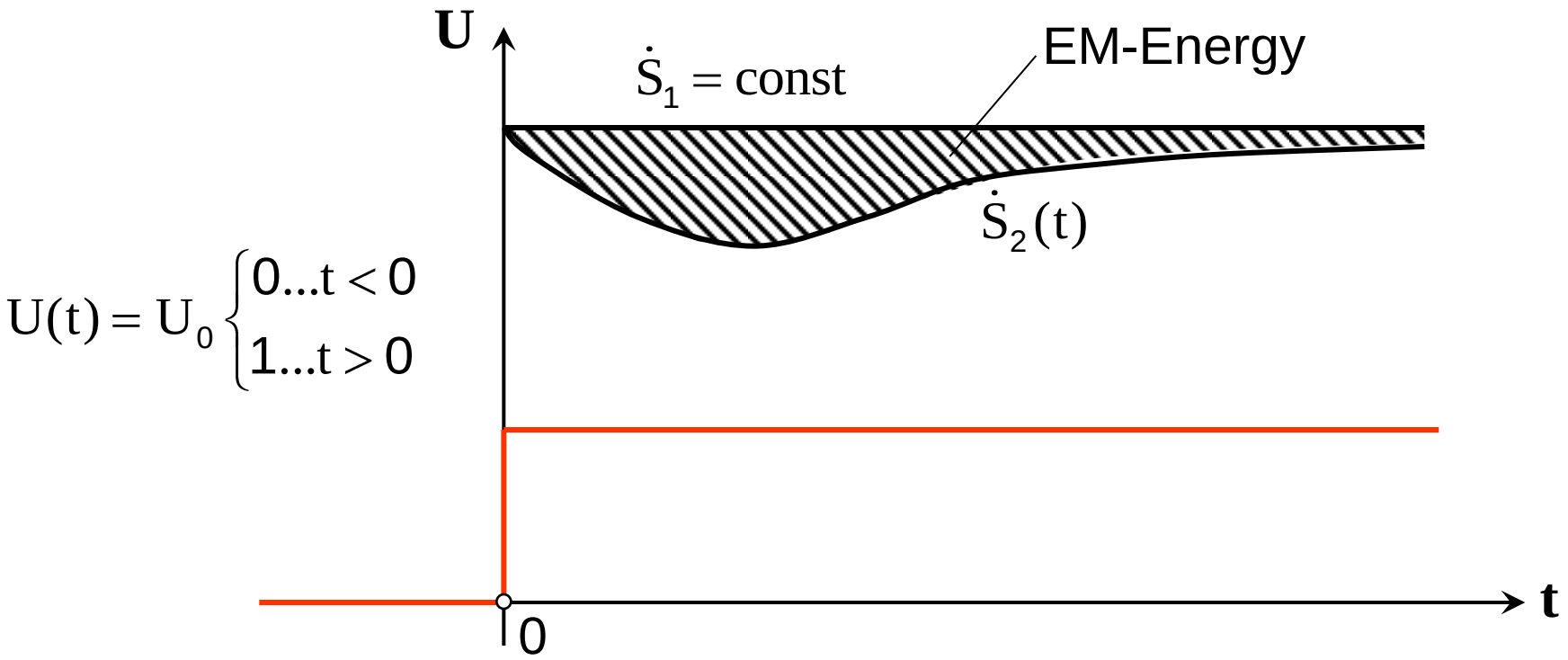
$$\frac{1}{Z_2} = \frac{1}{Z_{21}} + \frac{1}{Z_{22}},\ Z_{21} = R + pL,\ Z_{22} = R + \frac{1}{pC}$$

$$\rightarrow Z_2 = R$$

Adiabatic Electrical Networks ($N_1$, $N_2$)

Identical Impedance Functions ($Z_1$=$Z_2$=R)

Entropy Production in Response to Step-Stimulus-Function

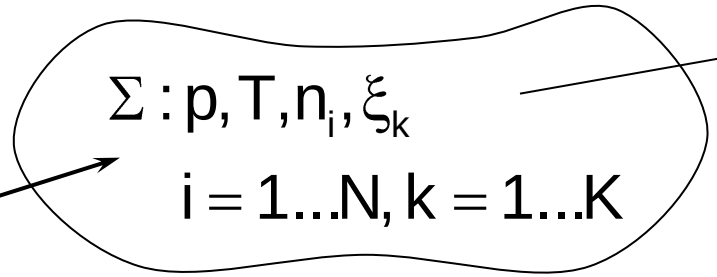



Ref.: J. Meixner, Thermodynamics and Network Theory, Opladen, 1969.

# 4. The Formalism of ETIP
# Thermodynamic System (W. Schottky, 1929)

Exchange processes ($\Sigma \leftrightarrow \Sigma^*$): heat, work, mass, …
Internal processes ($\Sigma$): chemical reactions etc.

$$\dot{n}^{(\alpha)} = \sum_{i=1}^{N} \dot{n}_i^{(\alpha)}$$




Internal variables
Bridgeman, Meixner,
Kestin, Flory

$$\dot{Q}, \dot{W} = -p^* \dot{V}$$

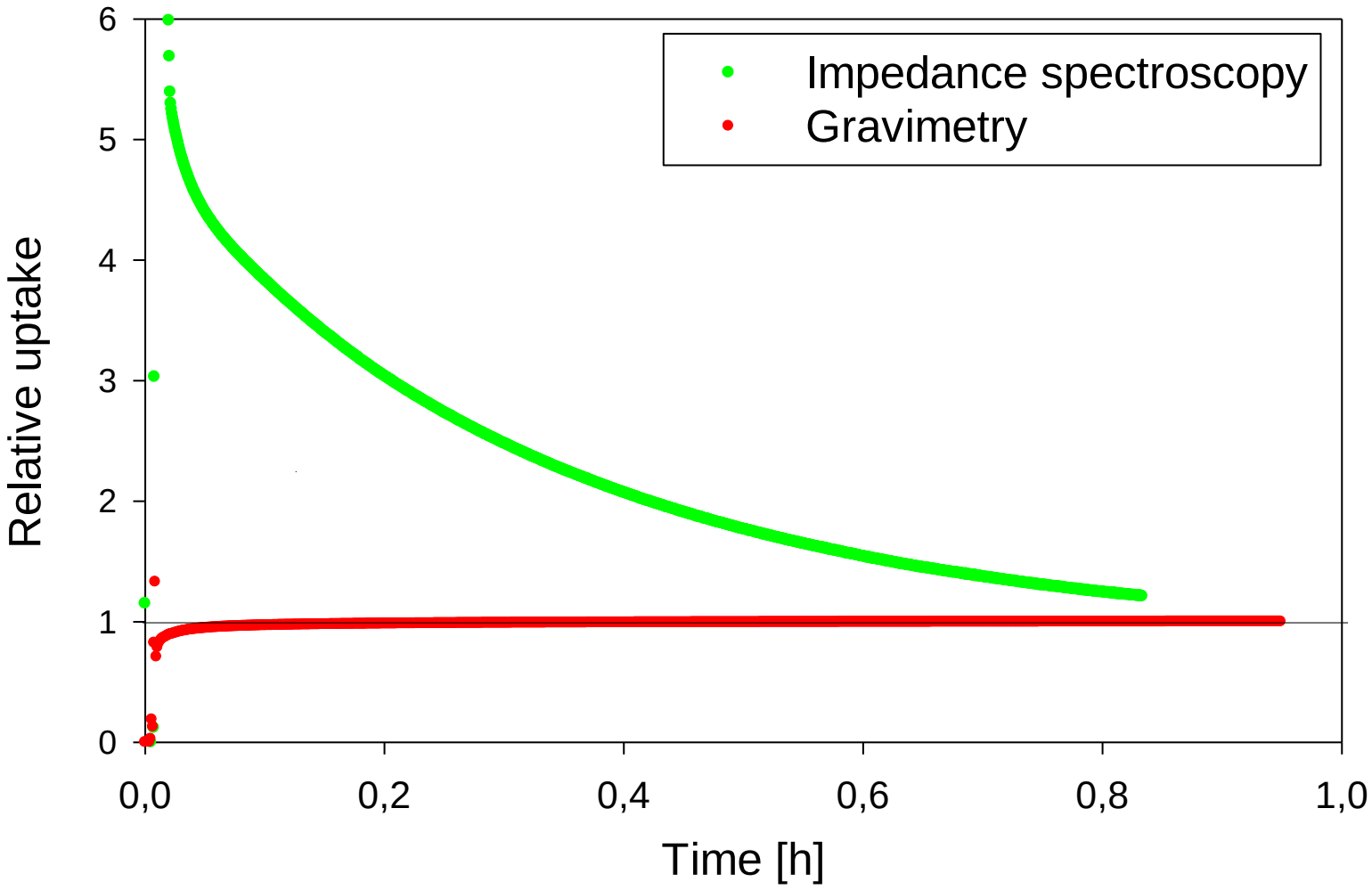
$$\Sigma^* : p^*, T^*, h^{(\alpha)}, s^{(\alpha)}, \mu_i^{(\alpha)}$$

$$\alpha = 1...A$$

Simple System: No external forces
surface phenomena
radiation effects
chemical reactions

# Internal Variables of Thermodynamic Systems, Examples

1. Glass: Transition Processes: amorphous phase $\rightarrow$ crystalline phase
2. Polymeric materials: Molecular relaxation processes
3. Gases & Liquids: Slow dissociation / recombination processes (radioactive decay) ($H_2S$/AC)
4. Liquid crystals: Phase transition processes
5. Dielectric-/Diamagnetic relaxation processes
6. Proteins in (ionic) solution: Structural- / Molecular-relaxation (denaturalization- i.e. folding, unfolding processes)




**Uptake curves of $H_2S$ on MS 13X, T=298K**

# Basic Laws of Thermodynamics (Σ)

0th Law: $p = p\left(T, c_1 = n_1/V \ldots c_N = n_N/V, \xi_1 \ldots \xi_k\right)$

1st Law: $U = U\left(T, V, n_1 \ldots n_N, \xi_1 \ldots \xi_k\right)$

$$dU = dQ - p^* dV + \sum_{\alpha=1}^{A} h^{(\alpha)} dn^{(\alpha)}$$

$$H = U + pV$$

$$dH = dQ + (p - p^*)dV + Vdp + \sum_{\alpha=1}^{A} h^{(\alpha)} dn^{(\alpha)}$$

# 2nd Law of Thermodynamics (Σ)

Equilibrium State (Z): $S = S(U, V, n_1 \ldots n_N, \xi_1 \ldots \xi_k)$

Clausius Inequality

$$S(Z) - S(Z_0) \geq \int_{Z_0}^{Z} \left( \frac{dQ}{T^*} + \sum_{\alpha=1}^{A} s^{(\alpha)} dn^{(\alpha)} \right)$$

Quasistatic changes of state ($Z \rightarrow Z + dZ$)

$$dS \geq \frac{dQ}{T^*} + \sum_{\alpha=1}^{A} s^{(\alpha)} dn^{(\alpha)}$$

# Gibbs Equation for $S = S(U, V, n_1 \ldots n_N, \xi_1 \ldots \xi_k)$

Quasistatic reversible changes of state $(T = T^*, p = p^*, \mu_i^{(\alpha)} = \mu_i)$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum_{i=1}^{N}\frac{\mu_i}{T}dn_i + \sum_{k=1}^{k}\frac{A_k}{T}d\xi_k$$

Equation of State (EOS) : $(./.) \equiv (U, V, n_1 \ldots n_N, \xi_1 \ldots \xi_k)$

Caloric $$\frac{1}{T} = \frac{1}{T(./.)} = \left(\frac{\partial S}{\partial U}\right)_{V,n,\xi}$$

Thermal $$\frac{p}{T} = \frac{p(./.)}{T(./.)} = \left(\frac{\partial S}{\partial V}\right)_{U,n,\xi}$$

Chemical $$-\frac{\mu_i}{T} = -\frac{\mu_i(./.)}{T(./.)} = \left(\frac{\partial S}{\partial n_i}\right)_{U,V,\xi}$$

Internal $$\frac{A_k}{T} = \frac{A_k(./.)}{T(./.)} = \left(\frac{\partial S}{\partial \xi_k}\right)_{U,V,n}$$

$$S(U,n_1...n_N) = S^* + \sum_{i=1}^{N} c_{i0} \ln\left(1 + \frac{U-U^*}{cnT^*}\right) n_i$$

$$S(U^*,n_1...n_N) \equiv S^* = \sum_{i=1}^{N} (s_{i0}^* - R\ln x_i) n_i$$

---

$$G(T,n_1...n_N) = G^* + \sum_{i=1}^{N} \left[ (c_{i0} - s_{i0}^* + R\ln x_i)(T-T^*) - c_{10} T \ln\left(\frac{T}{T^*}\right) \right] n_i$$

$$G(T^*,n_1...n_N) \equiv G^* = \sum_{i=1}^{N} (-s_{i0}^* + R\ln x_i) T^* n_i + U^* + pV$$

---

$$U = \sum_i U_{i0} = U^* + \sum_{i=1}^{N} c_{i0}(T-T^*) n_i \;,\; V = \sum_{i=1}^{N} v_{i0} n_i$$

$$H = \sum_i H_{i0} = H^* + \sum_{i=1}^{N} \left[ c_{i0}(T-T^*) + p v_{i0} \right] n_i$$

$$\mu_i(T,n_1...n_N) = \mu_i^* + (T-T^*) s_{i0}^* + c_{i0} T \ln\left(\frac{T}{T^*}\right) - R(T-T^*)\ln x_i$$

$$\mu_i(T^*,n_1...n_N) \equiv \mu_i^* = T^* s_{i0}^* - R T^* \ln x_i$$

**Incompressible, ideal fluid mixture** $(c_{i0} = \text{const}, v_{i0} = \text{const}, i = 1...N)$

# Gibbs Equation for $G = G(T, p, n_1 \dots n_N, \xi_1 \dots \xi_k)$

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i - \sum_{k=1}^{K} A_k d\xi_k$$

Chemical reactions ($Q \leqq N - E$)

$$C_i = \sum_{e=1}^{E} \alpha_{ie} E_e \,, \qquad \sum_{i=1}^{N} \nu_{iq} C_i = 0 \,, \qquad q = 1 \dots Q$$

Conservation of atomic numbers:

$$\sum_{i=1}^{N} \nu_{iq} \alpha_{ie} = 0 \,, \qquad e = 1 \dots E \,, \qquad q = 1 \dots Q$$

Chemical production of component (i):

$$n_i^c = n_i^* + \sum_{q=1}^{Q} \nu_{iq} (\gamma_q - \gamma_q^*) \,, \qquad i = 1 \dots N$$

# Gibbs Equation (T = const, p = const)

$$dG = -\sum_{q=1}^{Q} A_q^c d\gamma_q - \sum_{k=1}^{K} A_k d\xi_k$$

$$A_q^c = -\sum_{i=1}^{N} \mu_i \nu_{iq}$$

a) Restricted or frozen equilibria: = const … arbitrary value

$$A_q^c(T,p,\gamma_1 ... \gamma_Q, \xi_1 ... \xi_k) = 0\,, \qquad q = 1...Q$$

$$\rightarrow \qquad \gamma_{qE} = \gamma_q(T,p,\xi_1 ... \xi_k)$$

b) Full or unrestricted equilibria:

$$A_q^c(T,p,\gamma_1 ... \gamma_Q, \xi_1 ... \xi_K) = 0\,, \qquad q = 1...Q$$

$$A_k(T,p,\gamma_1 ... \gamma_Q, \xi_1 ... \xi_K) = 0\,, \qquad k = 1...K$$

$$\rightarrow \qquad \gamma_{qE} = \gamma_q(T,p)\,, \;\; \xi_{kE} ... \xi_k\,(T,p)$$

# Thermodynamics of Processes $(\Sigma \leftrightarrow \Sigma^*)$

## Fundamental Inequality (2nd Law (2), J. Meixner et al., 1970)

$$\Sigma: \quad \int_0^t \left\{ \left( \frac{1}{T} - \frac{1}{T^*} \right) \dot{U} + \left( \frac{p}{T} - \frac{p^*}{T^*} \right) \dot{V} + \sum_{q=1}^{Q} \frac{A_q^c}{T} \dot{\gamma}_q \right.$$

thermal energy work chemical reactions

$$\left. + \sum_{i,\alpha}^{NA} \left( \frac{\mu_i^{(\alpha)}}{T^*} - \frac{\mu_i}{T} \right) \dot{n}_i^{(\alpha)} - \sum_{k=1}^{K} \frac{A_k}{T} \dot{\xi}_k \right\} dt \geq 0 \quad \text{...all } t \geq 0$$

mass exchange internal processes

# Process Equations (Flux – Force – Relations)

Thermal energy $\dot{U} = F_u\,(./.)$

Mechanical work $\dot{V} = F_v\,(./.)$

Chemical reactions $\dot{\gamma}_q = \Gamma_q\,(./.) \qquad q = 1...Q$

Mass transfer $\dot{n}_i^{(\alpha)} = F_i^{(\alpha)}\,(./.) \qquad i = 1...N,\ \alpha = 1...A$

Internal processes $\dot{\xi}_k = \Xi_k\,(./.) \qquad k = 1...K$

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$$(./.) = \left( \frac{1}{T} - \frac{1}{T^*}, \frac{p}{T} - \frac{p^*}{T^*}, \frac{A_q^c}{T}, \frac{\mu_i^{(\alpha)}}{T^*} - \frac{\mu_i}{T}, \frac{A_k}{T} \right)$$

# Process Calculation (Initial value problem, ODE)

$$\Sigma: \quad Z(t) = \left( U(t)\,,\, V(t)\,,\, n_i(t) = \sum_{\alpha}^{A} n_i^{(\alpha)} + \sum_{q=1}^{Q} \nu_{iq}\gamma_q + n_i^{*}\,,\; \xi_k(t) \right)$$

Accompanying equilibrium intensive parameters:

$$S = S(U, v, n_i \ldots n_N, \xi_1 \ldots \xi_k)$$

$$\rightarrow \qquad T(t)\,,\, p(t)\,,\, \mu_i(t)\,,\, A_k(t)$$

Process equations for $\dot{U}, \dot{V}, \dot{n}_i, \dot{\xi}_k$, Taylor-series expansion:

$$\Sigma: \quad Z(t+\Delta t) = \left( U(t+\Delta t) = U(t) + F_u(t)\Delta t + \frac{1}{2}\dot{F}_u(\Delta t)^2 + \ldots \right.$$

...

$$\left. \xi_k(t+\Delta t) = \xi_k(t) + \Xi_k(t)\Delta t + \frac{1}{2}\dot{\Xi}(t)(\Delta t)^2 + \ldots \right)$$

Iteration procedure

# Isothermal and Isobaric Processes $(T = T^*, p = p^*)$

## Fundamental Inequality

$$\int_0^t \left\{ \sum_{q=1}^{Q} A_q^c \dot{\gamma}_q + \sum_{i\alpha}^{NA} (\mu_i^{(\alpha)} - \mu_i) \dot{n}_i^{(\alpha)} - \sum_{k=1}^{K} A_k \dot{\xi}_k \right\} dt \geq 0 \quad \text{...all } t \geq 0$$

## Process Equations (Flux – Force – Relations)

Chemical reactions : $\dot{\gamma}_q = \Gamma_q(./.), q = 1...Q$

Mass transfer : $\dot{n}_i^{(\alpha)} = F_i^{\alpha}(./.), i = 1...N, \alpha = 1...A$

Internal processes : $\dot{\xi}_k = \Xi_k(./.), k = 1...K$

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$$(./.) = (T = \text{const}, p = \text{const}, A_q^c = -\sum_i^N \mu_i \nu_{iq}, \mu_i^{(\alpha)} - \mu_i, A_k, i = 1...N, k = 1...K)$$

# Process calculation (Initial value problem, ODE)

$$\Sigma: \quad Z(t) = \left( T = \text{const}, p = \text{const}, n_i = n_{i0} + \sum_{\alpha=1}^{A} n_i^{(\alpha)} + \sum_{q=1}^{Q} \nu_{iq} \gamma_q \, , \xi_1 \ldots \xi_k \right)$$

Accompanying equilibrium intensive parameters:

$$G = G \;\; T = \text{const}, p = \text{const}, n_1 = n_N \, , \xi_1 \ldots \xi_k$$

$$\rightarrow \qquad \mu_i(t) \rightarrow A_q^C \;\; t \;\; , A_k(t)$$

Process equations for $\dot{\gamma}_q$ , $\dot{n}_i^{(\alpha)}$ , $\dot{\xi}_k$ , Taylor-series expansion:

$$\Sigma: Z(t+\Delta t) = \left( T = \text{const}, p = \text{const}, n_i(t+\Delta t) = n_i(t) + \sum_{\alpha}^{A} F_i^{(\alpha)} \Delta t + \sum \nu_{iq} \Gamma_q \Delta t + \ldots \right.$$

$$\left. \xi_k(t+\Delta t) = \xi_k(t) + \frac{1}{2} \Xi_k \Delta t + \frac{1}{2} \dot{\Xi} (\Delta t)^2 + \ldots \right)$$

Iteration procedure

# Classification of Process Equations

| F(%) | Linearity | Non-Linearity |
|---|---|---|
| Function (t) | TIP | NTIP |
| Functional (-∞<s≤t) | LPS | NPS (?) |

Fundamental Inequality 2nd Law, (*)
Theorem JUK, 1968

$$\int_0^t \sum_i^N \dot{x}_i F_i\ \underline{x}, \underline{\dot{x}}\ dt \geq 0 \ \text{... all } t \geq 0$$

$$F_i\ \underline{x}, \underline{\dot{x}} = 0\ = 0\ , i = 1...N$$

$$\rightarrow\ P_s = \sum_i^N \dot{x}_i F_i\ \underline{x}, \underline{\dot{x}}\ \geq 0$$

TIP

$$F_i\ \underline{x}, \underline{\dot{x}}\ = \sum_k^N L_{ik}\ \underline{x}\ \dot{x}_k$$

Onsager-Casimir-Relations

$$L_{ik} = \varepsilon_i \varepsilon_k L_{ki}\ ,\ \varepsilon_i, \varepsilon_k = \pm 1$$

NTIP

$$F_i\ \underline{x}, \underline{\dot{x}}\ = \sum_k^N L_{ik}\ \underline{x}\ \dot{x}_k + \sum_{klm} M_{iklm}\ \underline{x}\ \dot{x}_k \dot{x}_l \dot{x}_m + 0 \quad 5$$

LPS

$F_i\ \underline{x}, \underline{\dot{x}}$ ... Linear Passive Functional
(J. Meixner, H. König, 1964)

# Dimensional Analysis
# Phenomenological Coefficients and Functions:

Buckingham's Theorem (π – Theorem):

$$Y = Y(Z_1 ... Z_M)$$

Basic Units System (SI-System)

$$G_1, G_2, \ldots G_g$$

$$\rightarrow \; Y = \prod_{i=1}^{M} Z_i^{\alpha_i} \phi(\pi_1 ... \pi_{M-r})$$

$$Y = \left[ \prod_{i=1}^{M} Z_i^{\alpha_i} \right]$$

$$\pi_k = \prod_{j=1}^{M} Z_j^{\beta jk} \quad , \quad \pi_k = 1$$

$$\ln \phi = \phi_0 + \sum_{i=1}^{\mu - r} \phi_{1i} \ln \pi_i + \ldots$$

Dimensional Matrix

| | $Z_1$ | . . . . . | $Z_M$ |
|---|---|---|---|
| $G_1$ | $\zeta_{11}$ | . . . . . | $\zeta_{1M}$ |
| . | . | | |
| . | . | Rank: | |
| . | . | r | |
| . | . | | |
| . | . | | |
| $G_g$ | $\zeta_{g1}$ | . . . . . | $\zeta_{gM}$ |

# Dimensional Analysis

Taylor series expansion of the reduced function $\phi\ \pi_1 ... \pi_{M-r}$ :

$$\ln \phi\ \pi_1 ... \pi_{M-r} = \psi\ \ln \pi_1 ... \ln \pi_{M-r} \qquad ... \pi_i \geq 0$$

$$= \psi_0 + \sum_{i}^{M-r} \beta_i \ln \pi_i + \sum_{i,k}^{M-r} \gamma_{ik} \ln \pi_i \cdot \ln \pi_k + O\ 3$$

$$\phi\ \pi_1 ... \pi_{M-r} = C \prod_{i}^{M-r} \pi_i\ **\ \beta_i + \sum_{k} \gamma_{ik} \ln \pi_k + \sum_{k,l} \delta_{ikl} \ln \pi_k \cdot \ln \pi_l + ...$$

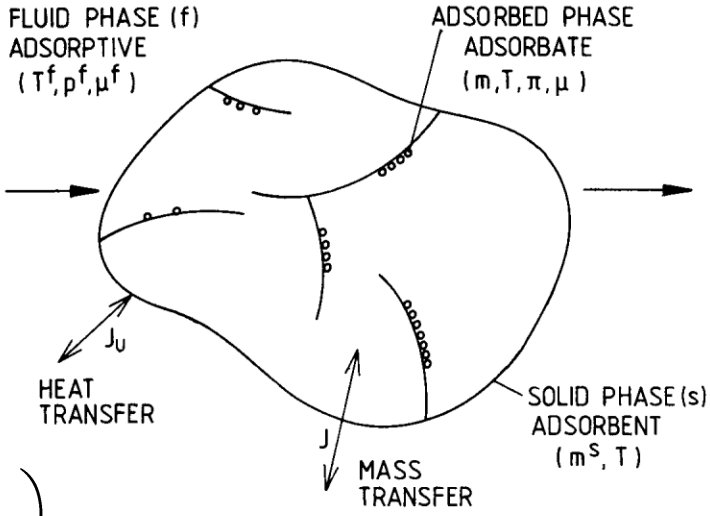
$$\cong C \prod_{i}^{M-r} \pi_i^{\beta_i} \prod_{i}^{M-r} \pi_i^{\sum_k \gamma_{ik} \ln \pi_k} ... \quad , \qquad C \doteq e^{\psi_0}$$

Energy: Scale shift invariance!

# Example 3: Non-Isothermal Gas Adsorption Processes

1st Law: $\dot{m}^{sa} = \dot{m}^{s} + \dot{m}^{a} = J$

$$\dot{U}^{sa} = \dot{U}^{s} + \dot{U}^{a} = J_u + h^f J$$




2nd Law:

$$\int_{-\infty}^{\infty} \left( \left( \frac{1}{T} - \frac{1}{T^f} \right) J_u + \left[ \left( \frac{\mu^f}{T^f} - \frac{\mu}{T} \right) + h^f \left( \frac{1}{T} - \frac{1}{T^f} \right) \right] J \right) dt \geq 0$$

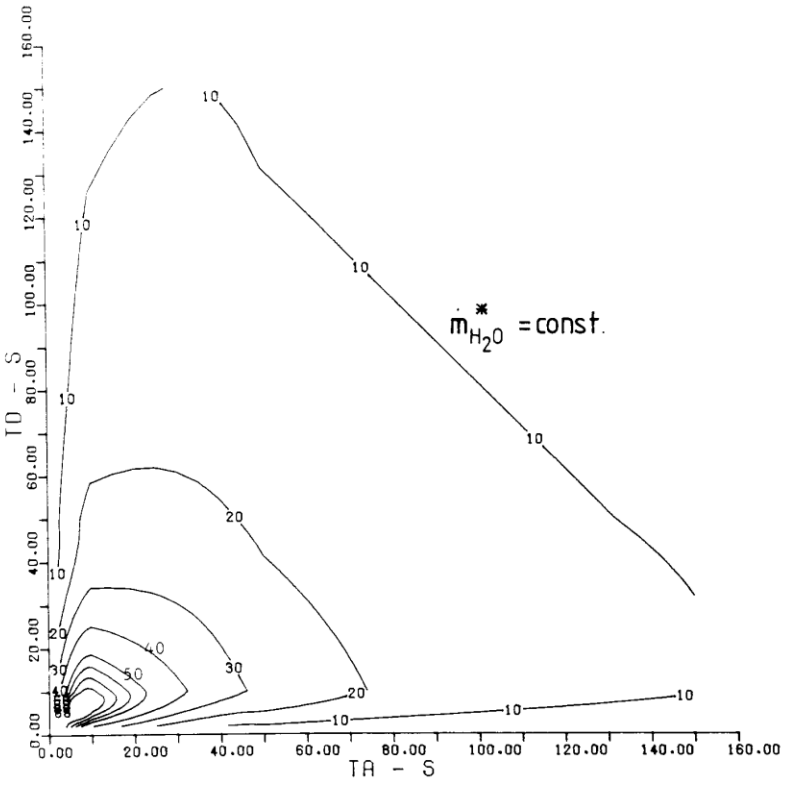
## Process Equations

$$\dot{m} = \beta A \left[ -c_p^f \ln\left( \frac{T^f}{T} \right) + R \ln\left( \frac{p^f}{p} \right) + h \left( \frac{1}{T} - \frac{1}{T^f} \right) \right] \qquad \dot{U}^{sa} = h^f - h^a \; \dot{m} + \alpha A_q \left( \frac{1}{T} - \frac{1}{T^f} \right)$$

Literature: J.U. Keller, Ber. Bunsenges. Phys. Chem. 91 (1987), p. 528.

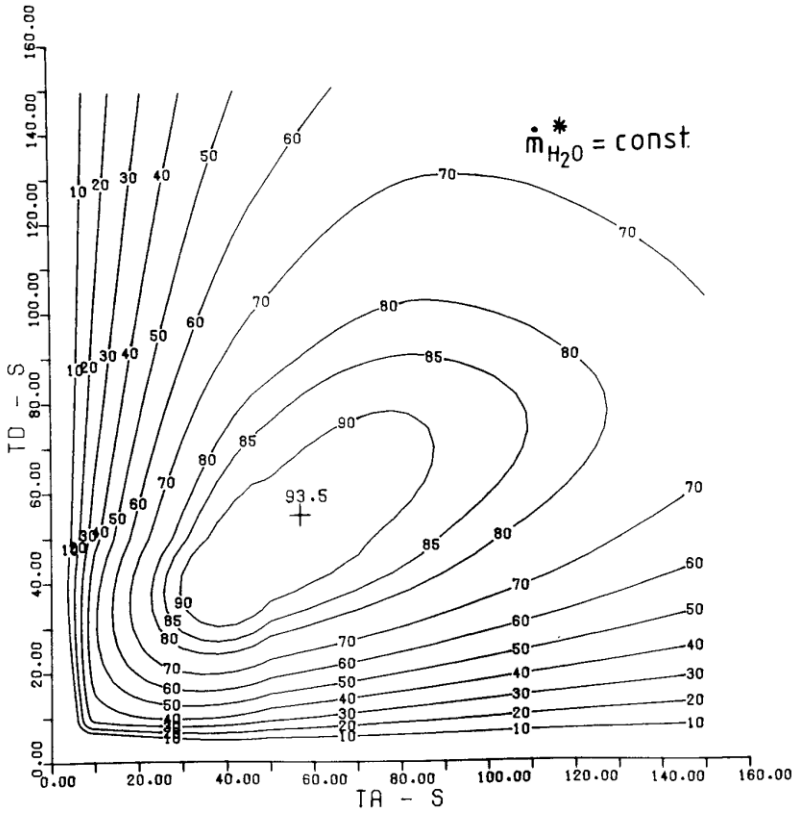
# Pressure Swing Adsorption Process (Water Vapor / Aerosorb LR4)

## Isothermal Process

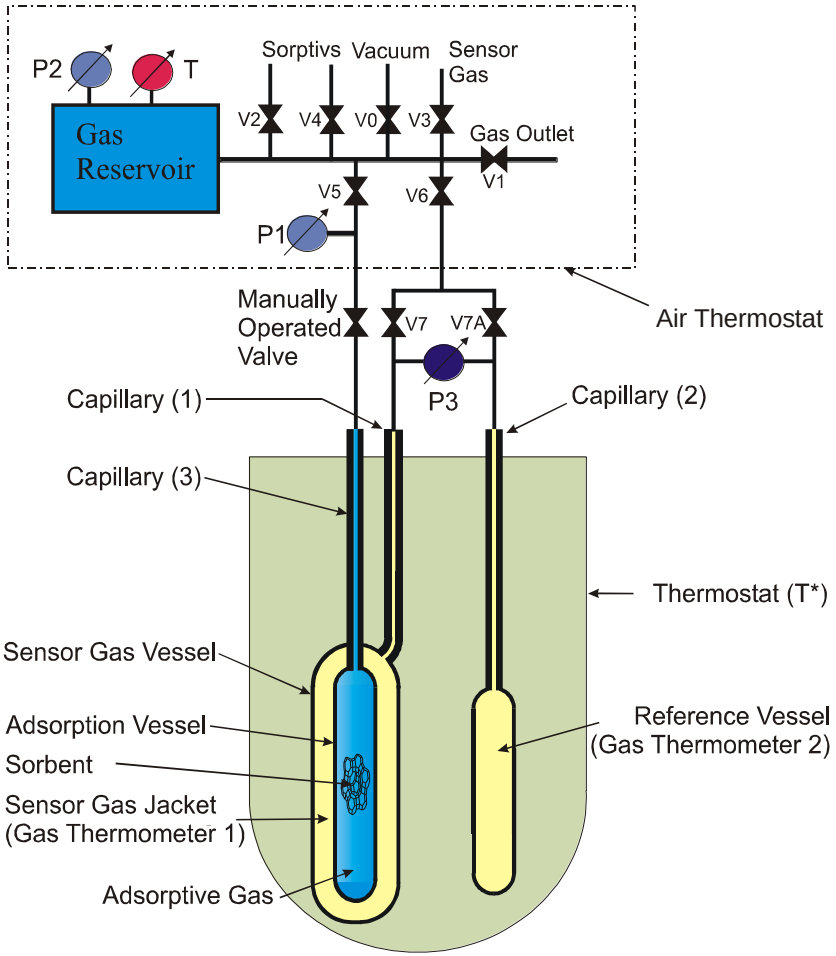



Dependence of the asymptotic mass flow $\dot{m}^*_{H20} = (m_{Ad}(t_A) - m_{De}(t_D))/(t_A + t_D)$ on the periods of adsorption ($t_A$) and desorption ($t_D$) for the isothermal process in units $10^{-1}$ g/s kg adsorbens. A maximum value seems to be approached for $t_A = t_D \to 0$.

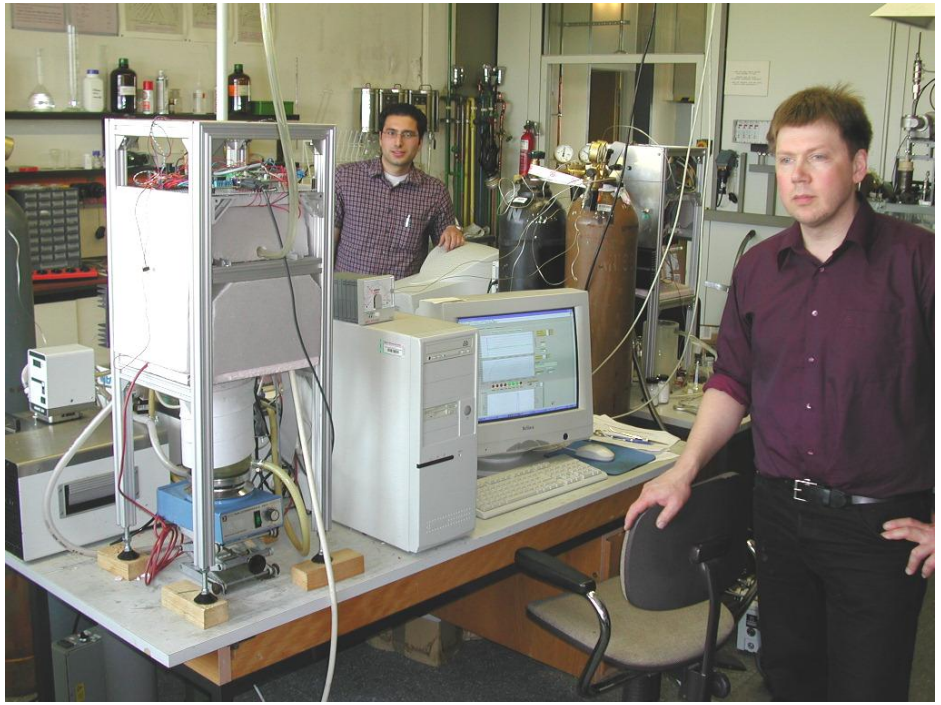
## Non-Isothermal Process




Dependence of the asymptotic mass flow $\dot{m}^*_{H20} = (m_{Ad}(t_A) - m_{De}(t_D)/(t_A + t_D)$ on the periods of adsorption ($t_A$) and desorption ($t_D$) for the non-isothermal process in units $10^{-2}$ g/s kg adsorbens. The maximum value $\dot{m}^*_{max} = 0.93$ g/s kg is realized for $t_A = 57$ s, $t_D = 53$ s.




Schematic diagram of a sensor gas calorimeter (SGC)

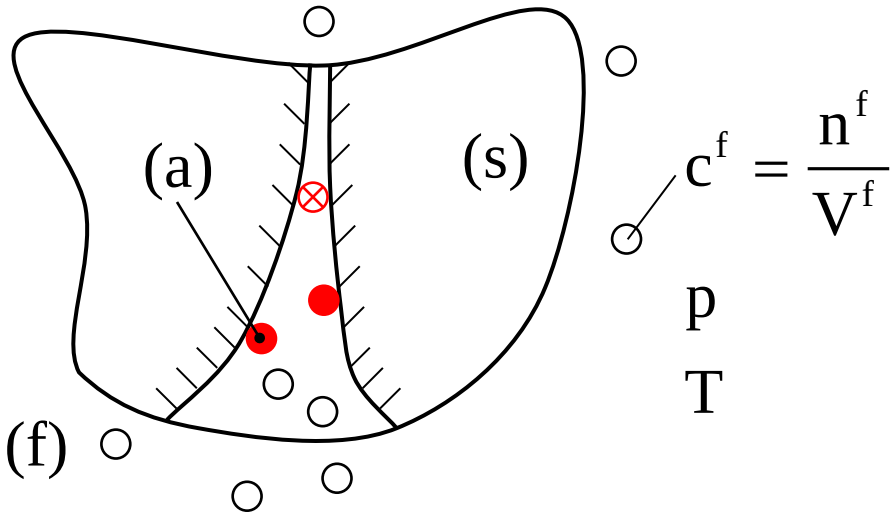


Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies.

# Example 3: Adsorption of Proteins (L)

## Basic Concepts

- Enzyme immobilization
- Biosensors, Diagnostics
- Biofouling, Contamination
- Drug targeting, controlled release
- Downstream processing Chromatography




Stationary Phase

Sorbent: $V^s = 1 - \varepsilon \; V_{part}$

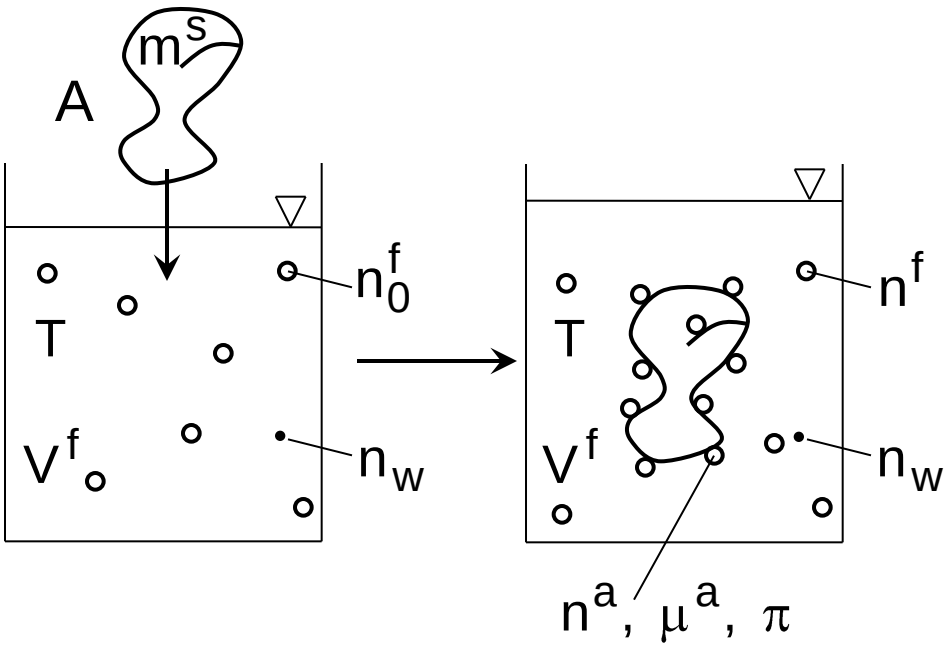
Mobile Phase

Sorbate $a, ipf$ : $V^a = \varepsilon V_{part}$

Sorptive $epf$ : $V^f = V^* - V_{part}$

Porosity : $0 \le \varepsilon \le 1$

# Liquid Phase Adsorption




Measurement methods ($c_0$,c):

- Spectroscopy
  Fluorescence
  Light scattering
  Light absorption
- Dielectric permittivity
- Calorimetry
  enthalpy, temperature
  heat capacity
- Release of ion, atomic groups etc. by protein upon adsorption

Protein molar balance

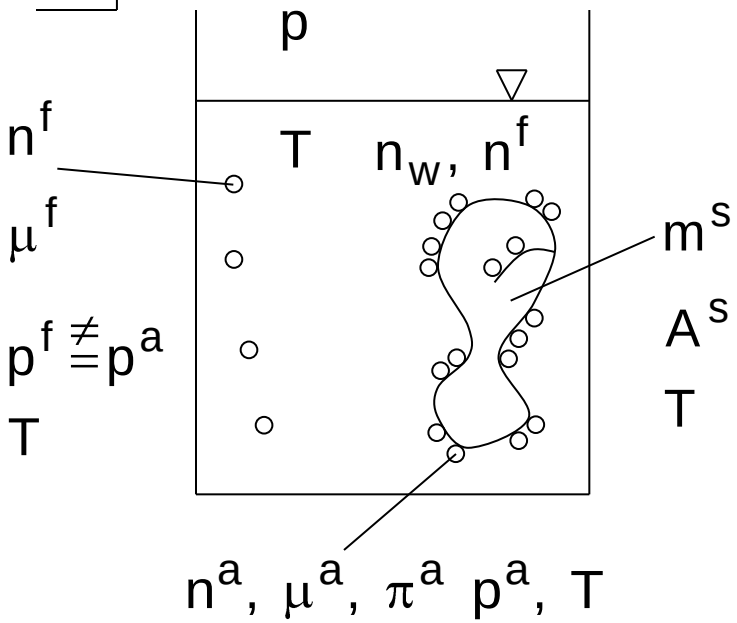
$$n_0^f = n^f + n^a \qquad 1$$

$$n_0^f = c_0 V_0^f$$

$$n^f = c V^f$$

$$n^a = c_0 V_0^f - c V^f \qquad 2 \qquad \rightarrow$$

$$n^a = n^a\ c, T, m^s \quad \text{... AI} \qquad 2a$$




Sorptive Sorbate Sorbent

Adsorption equilibrium:

$$\mu^f\ p^f,T\ = \mu^a\ \pi^a,T \qquad 1$$

## Protein Solution EOS

Protein/Water ≅ Ideal gas molecule/Vacuum

Osmotic pressure, dilute solutions

$$p^f = y^f p^* = y^f \frac{nRT}{V^f\ n^f,n_w,p,T} \qquad 2$$

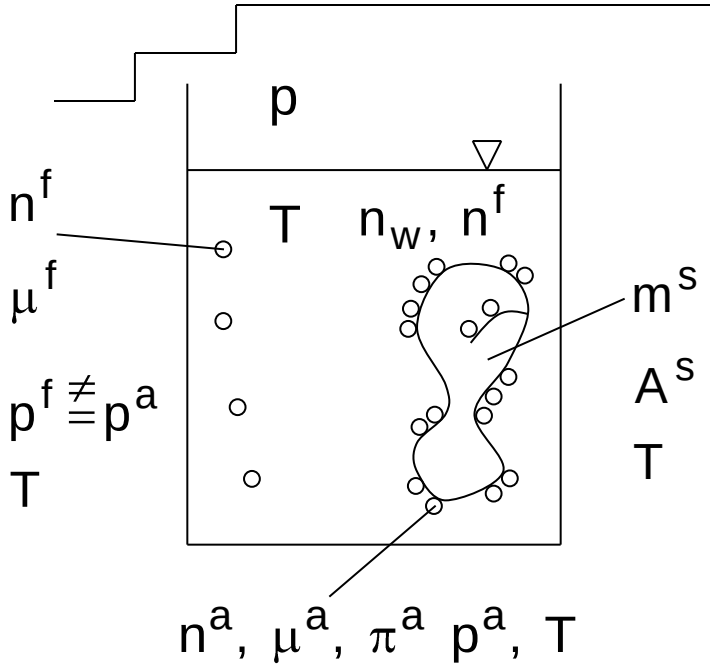
$$y^f = \frac{n^f}{n}\ ,\ n = n^f + n_w$$

$$\mu^f\ p^f,T\ = \mu^f\ p^+,T\ + RT\ln\left[\frac{f^f\ p^f,T}{p^+}\right] \qquad 3$$

$$f^f\ p^f,T\ = p^f\left[1 + B\ T\ p^f + C\ T\ p^{f2} + ...\right]$$

$$\cong p^f\ \text{... dilute solutions} \qquad 4$$

Kinetics of Protein Adsorption (N=1), Thermodynamic Model (1)




## Mass Transfer Process (TIP)

$$\dot{n}^a = \alpha A^s \left[ \mu^f \; p^f, T \; - \mu^a \; \pi^a, T \right] \qquad 7$$

$$1 : \mu^a \; \pi^a, T \; = \mu^f \; p^a, T$$

$p^a$ ... equiv. equilibrium pressure corresponding to n t

$$7,3,4 : \quad \dot{n}^a = \alpha A^s R T \ln p^f / p^a$$

$$2,6 : \quad \dot{n}^a \; t \; = \alpha A^s R T \ln \left[ \frac{y^f \; t \; p^* \; t}{\frac{1}{b} \cdot \frac{n^a / n^a_\infty}{1 - \; n^a / n^a_\infty}} \right]$$

Adsorption Isotherm / Equilibrium:

$$n^a = n^a_\infty \; T, m^s \; \frac{b p^a}{1 + b p^a} \qquad 5$$

$$p^a = \frac{1}{b} \cdot \frac{n^a / n^a_\infty \; T, m^s}{1 - \; n^a / n^a_\infty} \qquad 6$$

$$\dot{n}^a + \alpha A^s R T \ln \left[ \frac{1}{b} \cdot \frac{n^a / n^a_\infty}{1 - \; n^a / n^a_\infty} \right] = \alpha A^s R T \ln \left[ y^f \; \; p^* \; \; \right]$$

$n^a$ = $n^a_0$ ... initial adsorption

# Kinetics of Protein Adsorption (N=1), Thermodynamic Model (2)

# Entropy-free Thermodynamics of Processes (ETIP)

1. The concept of Clausius entropy is restricted to equilibrium states and can not be generalized unequivocally to non-equilibrium states. This has been demonstrated by using dynamically identical electric networks by J. Meixner already in 1970.

2. Thermodynamics of Processes in fluid Systems can be developed without using the concept of “non-equilibrium entropy”, i.e. a generalization of entropy to non-equilibrium states.

3. There are many processes of high engineering interest and practical relevance which can be described within the formalism of ETIP, especially in biotechnology and all its (coloured) branches.