4. Formalism of Entropy-free Thermodynamics of Processes
Thermodynamic System (W. Schottky, 1929)

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

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

$$\Sigma : p, T, n_i, \xi_k$$

$$i = 1...N, k = 1...K$$

Internal variables
Bridgeman, Meixner,
Kestin, Flory
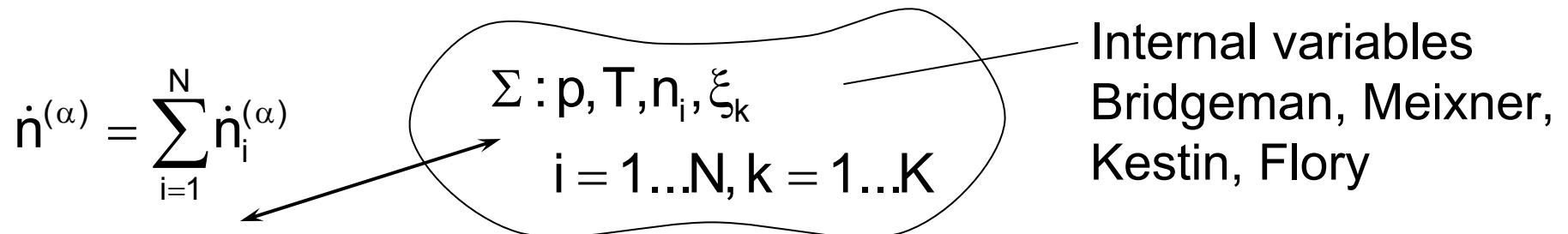
$$\dot{Q}, \dot{W} = -p^* \dot{V}$$

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

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

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

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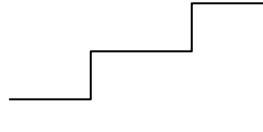
Internal Variables of
Thermodynamic Systems, Examples

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)

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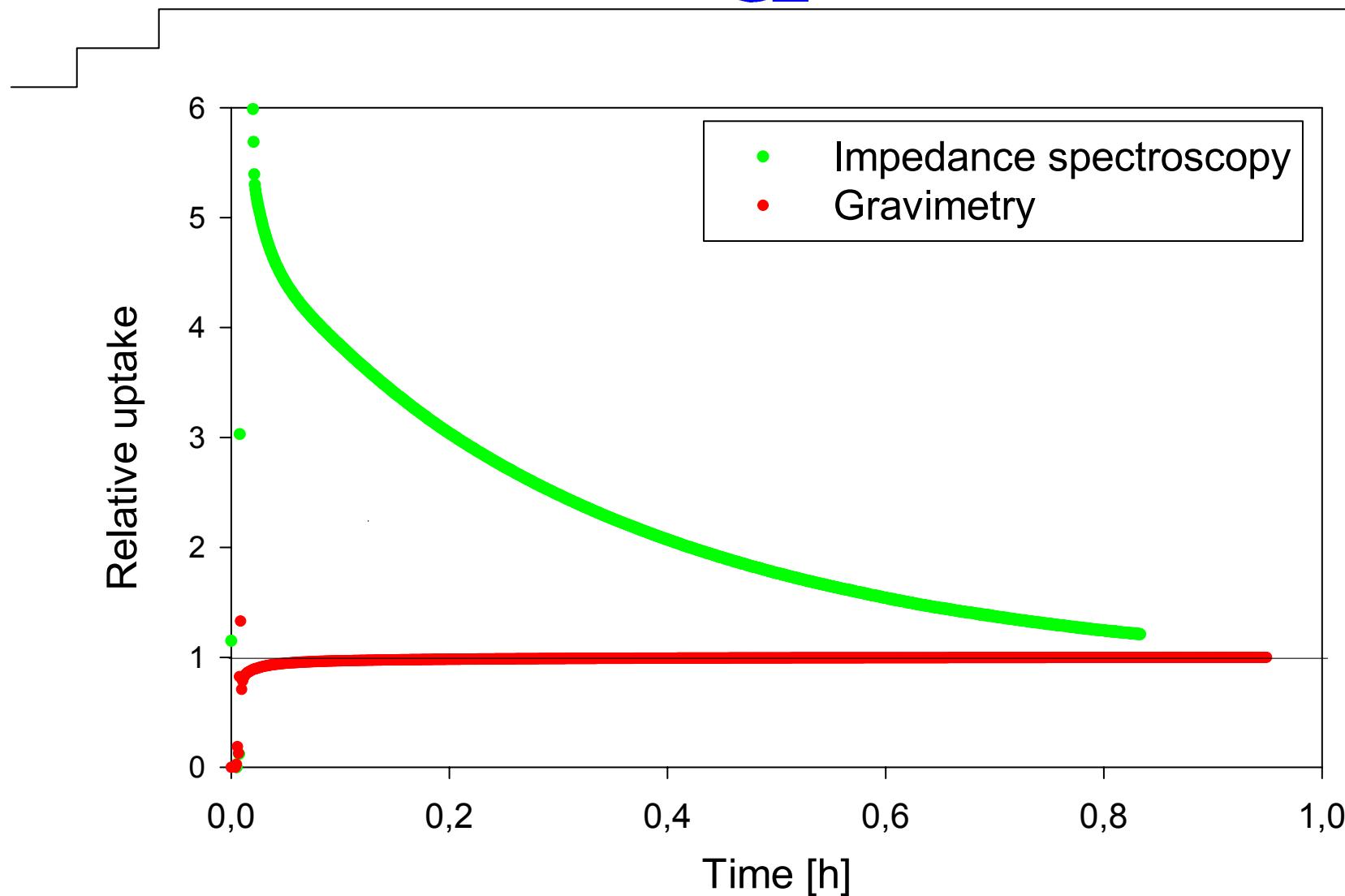
Uptake curves of H$_2$S on MS 13X, T=298K

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Basic Laws of Thermodynamics (Σ)

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

1st Law: $\quad U = U\,(T, V, n_1 ... n_N, \xi_1 ... \xi_k)$

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

$$H = U + pV$$

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

2nd Law of Thermodynamics (Σ)

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

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 … n_N, ξ_1 … ξ_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) : $(./.) \equiv (U, V, n_1...n_N, \xi_1...\xi_k)$

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

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

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

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

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

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

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

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

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

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

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Gibbs Equation for G = G (T, p, n_1 … n_N, ξ_1 … ξ_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)

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

Conservation of atomic numbers:

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

Chemical production of component (i):

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

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

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

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

b) Full or unrestricted equilibria:

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

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

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

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

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Process Equations (Flux – Force – Relations)

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

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

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

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

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

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

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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:

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

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

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

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

...

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

Iteration procedure

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

Fundamental Inequality

$$\int\limits_0^t \left\{ \sum_{q=1}^Q A_q^c \dot{\gamma}_q + \sum_{i\alpha}^{NA} (\mu_i^{(\alpha)} - \mu_i)\dot{n}_i^{(\alpha)} - \sum_{k=1}^K A_k \dot{\xi}_k \right\} dt \geq 0 \quad ...\text{all } t \geq 0$$

Process Equations (Flux – Force – Relations)

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

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

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

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

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Process calculation (Initial value problem, ODE)

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

Accompanying equilibrium intensive parameters:

$$G = G\left(T = const, p = const, n_1 = n_N, \xi_1...\xi_k \right)$$

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

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

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

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

Iteration procedure

Classification of Process Equations

F(%)		Linearity	Non-Linearity
	Function (t)	TIP	NTIP
	Functional ($-\infty < s \leq t$)	LPS	NPS (?)

Fundamental Inequality $\left(2^{nd}\ \text{Law, (*)}\right)$
Theorem $\left(\text{JUK, 1968}\right)$

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

$$F_i \left(\underline{x}, \underline{\dot{x}} = 0\right) = 0 \ , \ i = 1...N$$

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

TIP

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

Onsager-Casimir-Relations

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

NTIP

$$F_i \left(\underline{x}, \underline{\dot{x}}\right) = \sum_k^N L_{ik} \left(\underline{x}\right) \dot{x}_k +$$

$$+ \sum_{klm} M_{iklm} \left(\underline{x}\right) \dot{x}_k \dot{x}_l \dot{x}_m + 0 \ \ (5)$$

LPS

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

Example 4: Non-Isothermal Gas Adsorption Processes

1st Law: $\left(m^s + m^a\right)^{\cdot} = J$

$$\dot{U}^{sa} = \left(U^s - U^a\right)^{\cdot} = J_u + h^f J$$

FLUID PHASE (f)
ADSORPTIVE
(T^f, p^f, μ^f)

ADSORBED PHASE
ADSORBATE
(m, T, π, μ)

J_u

HEAT TRANSFER

J

MASS TRANSFER

SOLID PHASE (s)
ADSORBENT
(m^s, T)

2nd Law:

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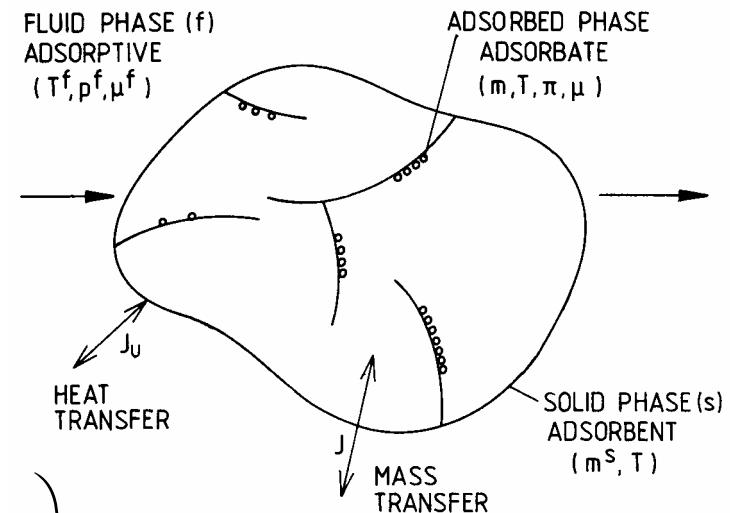
Process Equations

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

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

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Pressure Swing Adsorption Process (Water Vapor / Aerosorb LR4)

Isothermal Process
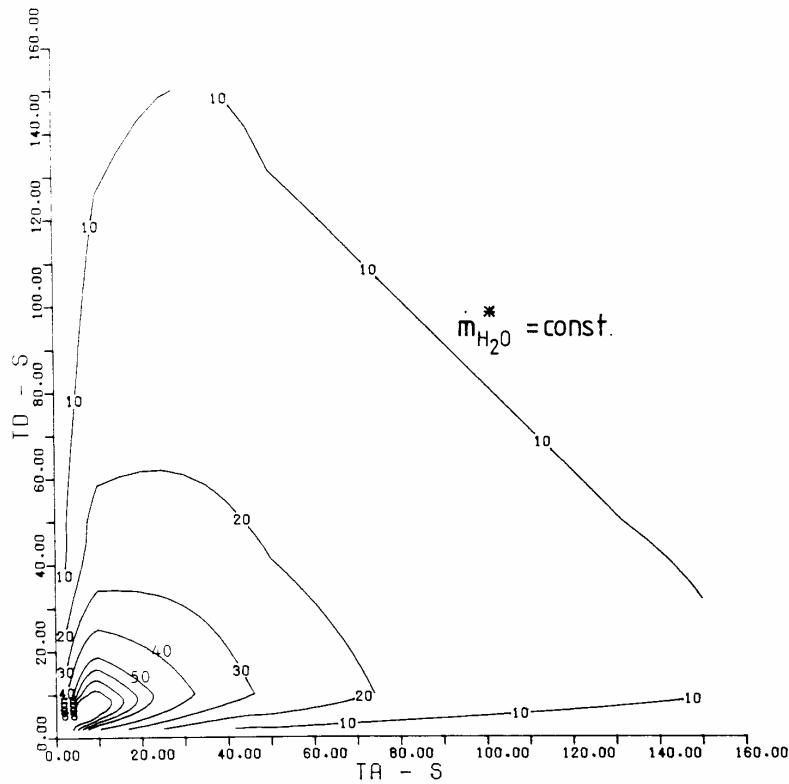
Non-Isothermal Process

Dependence of the asymptotic mass flow $\dot{m}_{H2O}^{*} = (m_{Ad}(t_A) - m_{De}(t_D))/(t_A + t_D)$ 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 $t_A = t_D \rightarrow 0$.
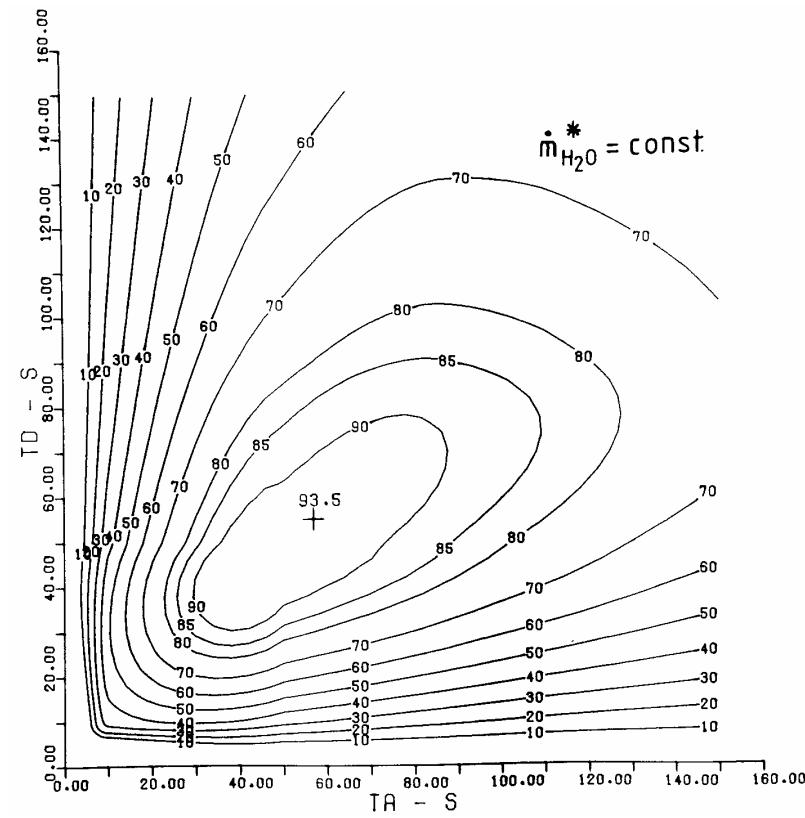
Dependence of the asymptotic mass flow $\dot{m}_{H2O}^{*} = (m_{Ad}(t_A) - m_{De}(t_D))/(t_A + t_D)$ on the periods of adsorption (t_A) and desorption (t_D) for the non-isothermal process in units 10^{-2} g/s kg adsorbens. The maximum value $\dot{m}_{\max}^{*} = 0.93$ g/s kg is realized for $t_A = 57$ s, $t_D = 53$ s.

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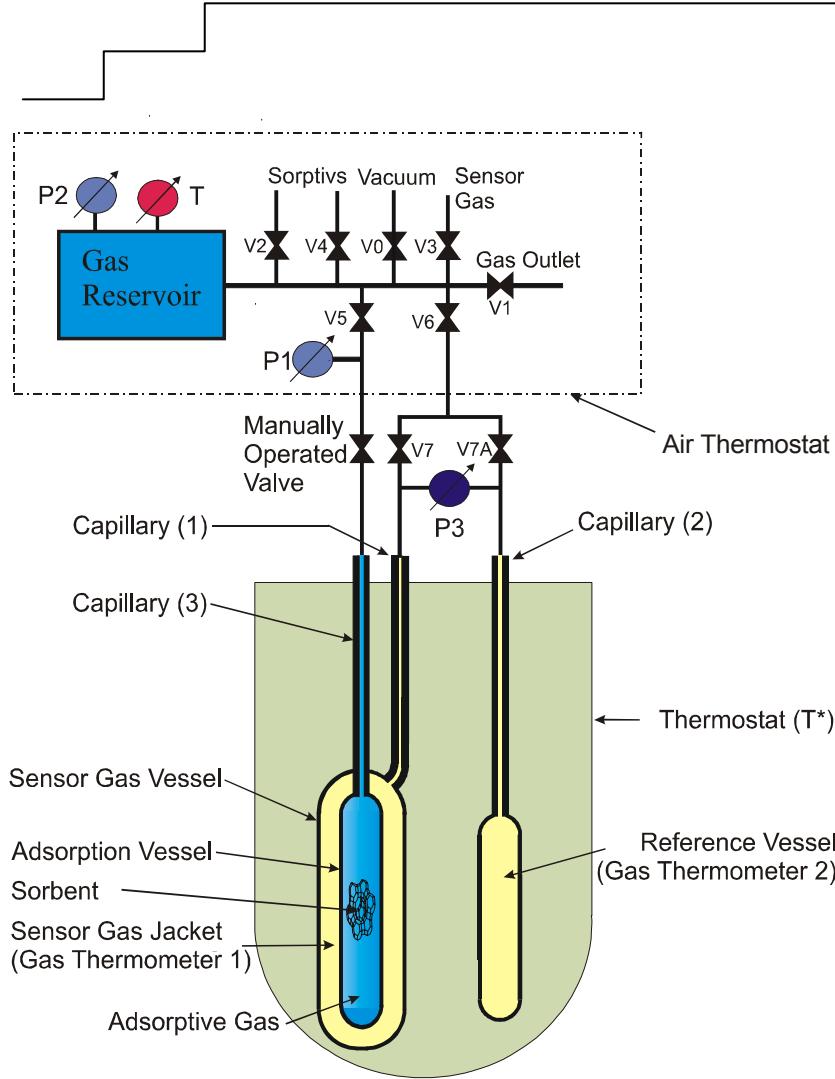
Schematic diagram of a sensor gas
calorimeter (SGC)
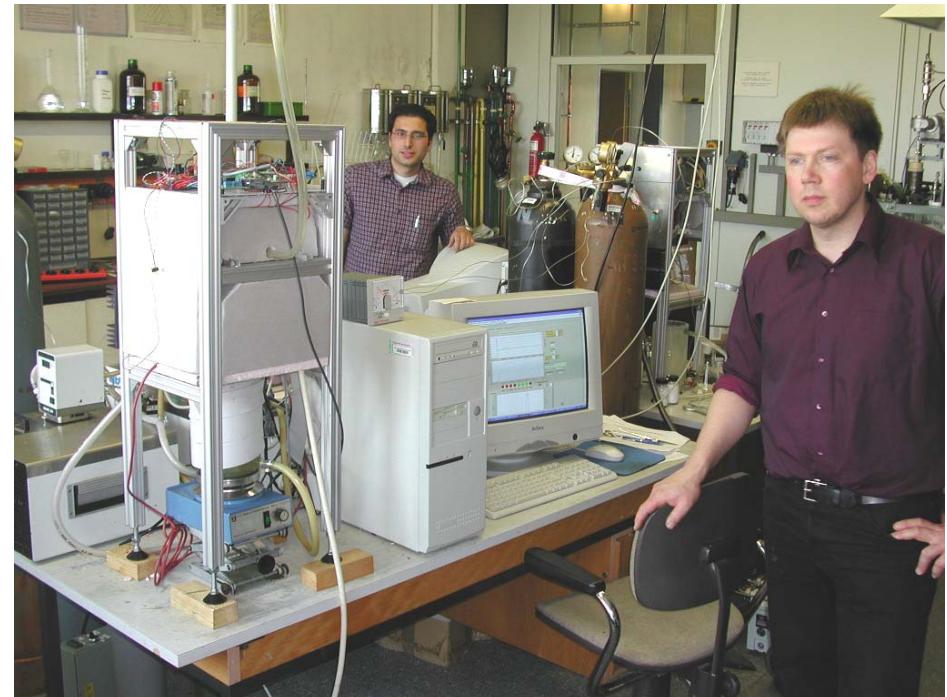
Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies. © IFT, University of Siegen, 2003.

Example 5: Adsorption of Proteins (L)   Basic Concepts

- Enzyme immobilization

- Biosensors, Diagnostics

- Biofouling, Contamination

- Drug targeting,
  controlled release

- Downstream processing
  Chromatography
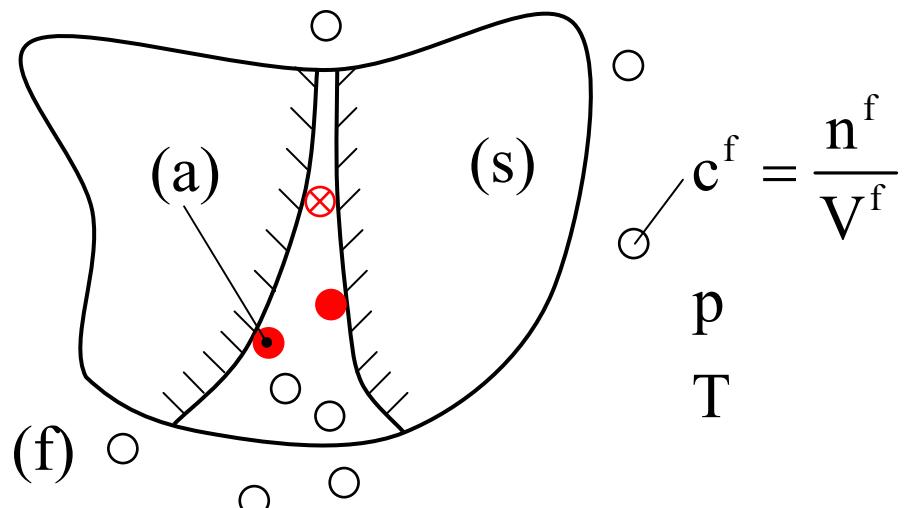
$$c^f = \frac{n^f}{V^f}$$

$$p$$

$$T$$

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   : $0 \leq \varepsilon \leq 1$

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Liquid Phase Adsorption

Measurement methods (c_0, c):

- Spectroscopy
  <u>Fluorescence</u>
  Light scattering
  Light absorption

- Dielectric permittivity

- Calorimetry
  enthalpy, temperature
  heat capacity

- Release of ion, atomic groups etc.
  by protein upon adsorption
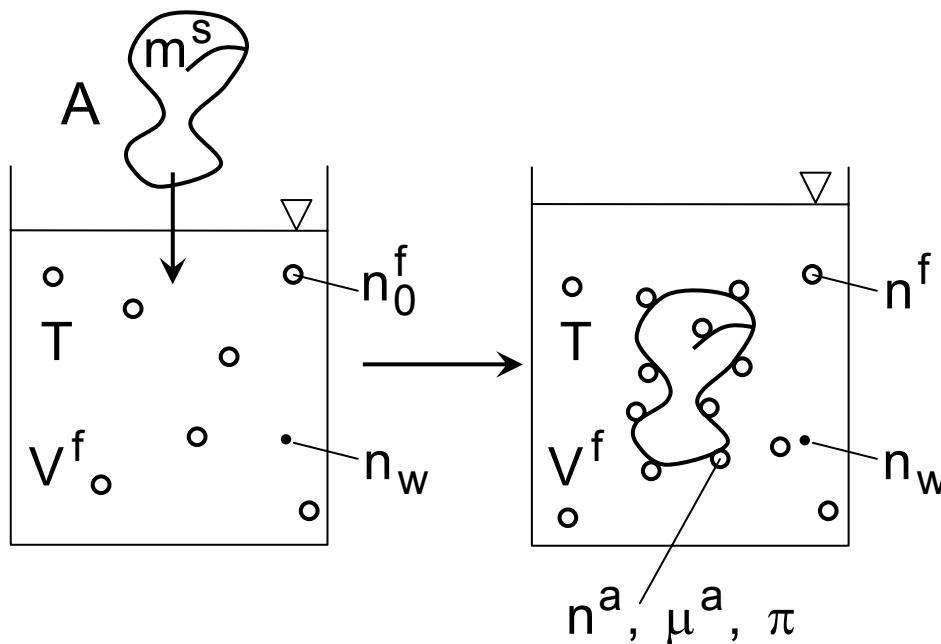
Protein molar balance

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

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

$$\underline{n^f = c\, V^f}$$

$$n^a = c_0 V_0^f - c\, V^f \qquad (2) \qquad \rightarrow \qquad n^a = n^a\left(c, T, m^s\right) \ \dots \ \text{AI} \qquad (2a)$$

Protein Solution EOS

n^f

$T \quad n_w, n^f$

m^s

μ^f

A^s

$p^f \neq p^a$

T

T

$n^a, \mu^a, \pi^a\left(p^a, T\right)$
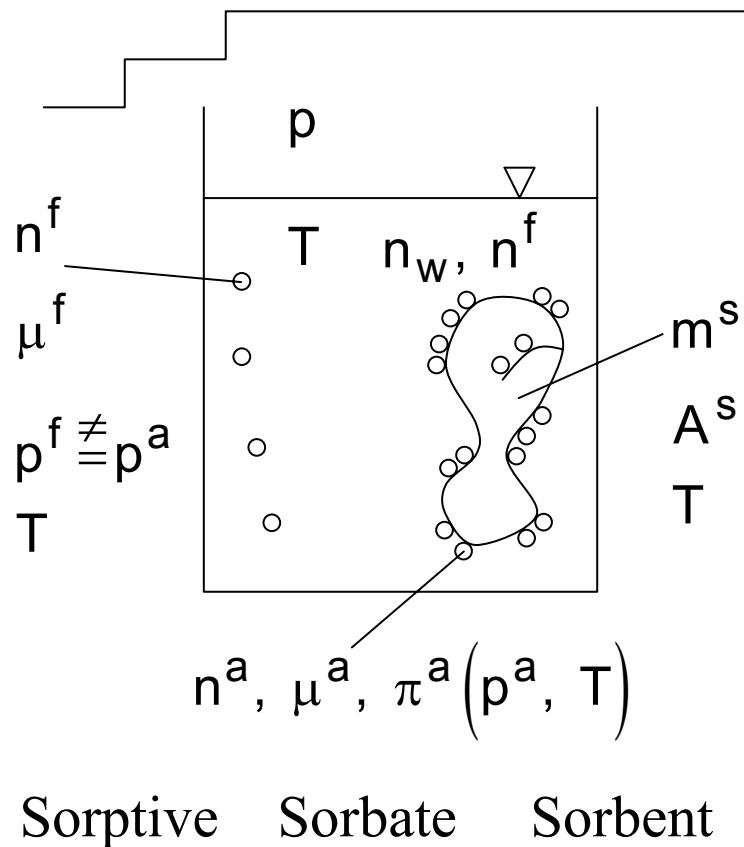
Sorptive   Sorbate   Sorbent

Adsorption equilibrium:

$$\mu^f\left(p^f, T\right) = \mu^a\left(\pi^a, T\right) \quad (1)$$

Protein/Water $\cong$ Ideal gas molecule/Vacuum
Osmotic pressure, dilute solutions

$$p^f = y^f p^* = y^f \frac{nRT}{V^f\left(n^f, n_w, p, T\right)} \quad (2)$$

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

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

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

$$\cong p^f \ ... \ \text{dilute solutions} \quad (4)$$

Kinetics of Protein Adsorption (N=1), Thermodynamic Model (1)
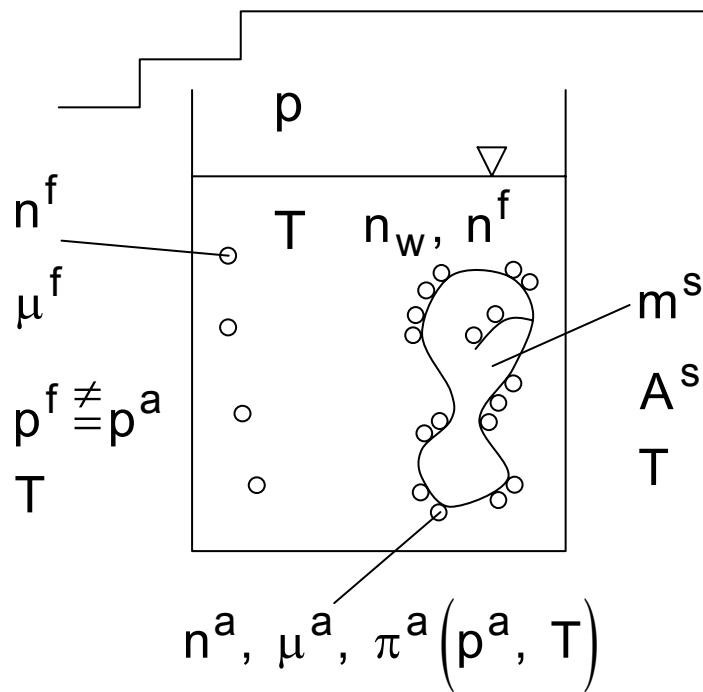
Mass Transfer Process (TIP)

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

$$(1): \quad \mu^a\left(\pi^a, T\right) = \mu^f\left(p^a, T\right)$$

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

$$(7,3,4): \quad \dot{n}^a = \alpha A^s RT \ln\left(p^f / p^a\right)$$

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

Adsorption Isotherm / Equilibrium:

$$n^a = n^a_\infty\left(T, m^s\right)\frac{bp^a}{1+bp^a} \qquad (5)$$

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

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

$$n^a(0) = n^a_0 \quad \text{... initial adsorption}$$

Diagram labels: n^f, μ^f, $p^f \neq p^a$, T, p, T n_w, n^f, m^s, A^s, T, $n^a, \mu^a, \pi^a\left(p^a, T\right)$

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

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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.