

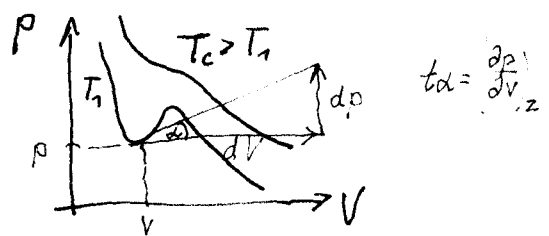
TD - fundamentals

1. Jacobi transformation

- EOS $P = P(T, V)$

$$dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV \quad (1)$$

e.g. vdW
 $P = \frac{RT}{V-b} - \frac{a}{V^2}$



$$dp = \left(\frac{R}{V-b}\right) dT + \left(-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\right) dV$$

- Differentials dT and dV in (1) are arbitrary, for given (T, V) they determine the value of dp .
- With the constraint $p = \text{const.}$ i.e. $dp = 0$, the differentials are no more arbitrary, they must fulfill the Eq.

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial(V, p)}{\partial(T, p)} = - \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = - \frac{\frac{\partial(p, V)}{\partial(T, V)}}{\frac{\partial(p, T)}{\partial(V, T)}} = 1$$

Jacobian notation for differential of T at constant p

$$\frac{1}{T} = \frac{\partial(p, V)}{\partial(T, V)} \cdot \frac{\partial(V, T)}{\partial(p, T)} = \frac{\partial(V, p)}{\partial(T, T)}$$

$$\begin{aligned} \partial(V, T) &= -\partial(T, V) \\ \partial(p, V) &= -\partial(V, p) \\ \text{etc.} \end{aligned}$$

Jacobi (1805...1851)
 (relations which are satisfied by differentials with constraints)

(2)

Application:

→ Prove that

$$\boxed{\frac{\chi_T}{\chi_S} = \frac{C_p}{C_v}} \quad (2)$$

where

$$\chi_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

isothermal compressibility

$$\chi_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

adiabatic compressibility

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

(molar) heat capacity at const. p

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

(molar) heat capacity at const. V

- Solution:

First, notice that $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$ and $C_v = T \left(\frac{\partial S}{\partial T} \right)_V$

Therefore, Eq. 2 rewrites in Jacobi notation

$$\frac{\chi_T}{\chi_S} = \frac{\frac{\partial(V,T)}{\partial(p,T)}}{\frac{\partial(V,T)}{\partial(p,S)}} \frac{\partial(p,S)}{\partial(V,S)} \stackrel{?}{=} \frac{\frac{\partial(S,p)}{\partial(T,p)} \frac{\partial(T,V)}{\partial(S,V)}}{\frac{\partial(S,p)}{\partial(T,p)} \frac{\partial(T,V)}{\partial(S,V)}} = \frac{[-\partial(p,S)] [-\partial(V,T)]}{[-\partial(p,T)] [-\partial(V,S)]} \text{ q.e.d.}$$

2. TD potentials, definition, properties

1. Law	$dU = \delta Q + \delta W$
2. Law	$\delta Q \leq TdS$ (*)

internal energy U

U is a state function,
 Q and W not.

For reversible process equality in(*) The entropy S is a state function

$$(\delta Q_{rev})_p = C_p dT$$

↑
heat capacity of the system at const. p

$$dS = \frac{\delta Q_{rev}}{T}$$

$$S(T_1, p_0) = S(T_0, p_0) + \int_{T_0}^{T_1} \frac{\delta Q_{rev}}{T}$$

differential volume-pressure work done upon the system

$\delta W = -pdV$

(Clausius inequality)

Therefore, differentials of U , S and V are related by

$dU = TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ <p style="text-align: center;"> \parallel T \parallel $-p$ </p>	(1)
---	-----

Equ. (1) is true when the composition of the system does not change (mol numbers n_1, n_2, \dots, n_c)

$U(S, V, n_1, n_2, \dots, n_c)$

c = number of different components

If the composition (n_1, n_2, \dots, n_c) changes, then we have

$dU = TdS - pdV + \sum_{k=1}^c \mu_k dn_k$	(2)
--	-----

$\mu_k \equiv \left(\frac{\partial U}{\partial n_k}\right)_{S, V, n_{i \neq k}}$
--

chemical potential of component k in the system

(4)

Internal energy U is an extensive function of state

$$(2) \quad U((1+\epsilon)S, (1+\epsilon)V, (1+\epsilon)n_1, (1+\epsilon)n_2, \dots, (1+\epsilon)n_c) = (1+\epsilon)U(S, V, n_1, \dots, n_c)$$

→ The increase of the system by a factor $(1+\epsilon)$ increases all extensive variables and functions by the same factor
 Equ. (2) gives after expansion (assuming $|\epsilon| \ll 1$)

$$U(S, V, n_1, n_2, \dots, n_c) + \epsilon \left[\left(\frac{\partial U}{\partial S} \right)_{S, n_k} S + \left(\frac{\partial U}{\partial V} \right)_{S, n_k} V + \sum_{k=1}^c \left(\frac{\partial U}{\partial n_k} \right)_{S, V, n_{k \neq i}} n_k \right] = (1+\epsilon)U$$

i.e. (c.f. Euler-theorem for homogeneous functions)

$$(3) \quad U(S, V, n_k) = \left(\frac{\partial U}{\partial S} \right)_{S, n_k} S + \left(\frac{\partial U}{\partial V} \right)_{S, n_k} V + \sum_{k=1}^c \left(\frac{\partial U}{\partial n_k} \right)_{S, V, n_{k \neq i}} n_k = T \cdot S - p \cdot V + \sum_{k=1}^c \mu_k n_k$$

$$\text{Define } \sum_{k=1}^c \mu_k n_k \equiv G$$

Gibbs energy of the system.

equ. (3)
rewrites

$$U = TS - pV + G \quad (3a)$$

We find the differential of G using 1.+2. Law of TD:

$$dU = TdS - pdV + \sum_k \mu_k dn_k$$

1.+2. Law see equ. (2)

$$dU = TdS + SdT - pdV - Vdp + \underbrace{\sum_k \mu_k dn_k + \sum_k n_k d\mu_k}_{dG} \quad \text{differential of (3a)}$$

i.e.

$$\sum_k n_k d\mu_k = -SdT + Vdp \quad (= 0 \text{ for isothermic-isobaric processes})$$

in general

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

$$\mu_k = \left(\frac{\partial G}{\partial n_k} \right)_{p, T, n_{i \neq k}} \quad \text{chemical potential}$$

$$G = G(p, T, n_K) = \sum_K n_K \mu_K = U + pV - TS$$

$$\mu_K = \left(\frac{\partial G}{\partial n_K} \right)_{p, T, n_{i \neq K}} = \left(\frac{\partial U}{\partial n_K} \right)_{S, V, n_{i \neq K}}$$

$$dG = dU + d(pV) - d(TS)$$

$$dG = \cancel{TdS} - \cancel{pdV} + \sum_K \mu_K dn_K + \cancel{pdV} - \cancel{TdS} + Vdp - SdT$$

$$dG = \sum_K \mu_K dn_K + \sum_K n_K d\mu_K = \sum_K \mu_K dn_K + Vdp - SdT$$

At const. p, T

$$dG = \sum_K \mu_K dn_K$$

$$\text{and } \sum_K n_K d\mu_K = 0$$

in general:

$$dG = \sum_K \mu_K dn_K + Vdp - SdT$$

$$\sum_K n_K d\mu_K = Vdp - SdT \quad \text{Gibbs-Duhem}$$

⑥ → Enthalpy

$$H \equiv U + pV = (TS - pV + G) + pV = G + TS$$

$$dH = d(U + pV) = TdS - p dV + \sum_k \mu_k dn_k + p dV + V dp$$

$$dH = TdS + Vdp + \sum_k \mu_k dn_k$$

One can obtain H using Euler's theorem

$$H = H(S, p, n_k) \stackrel{\text{(Euler)}}{=} \left(\frac{\partial H}{\partial S} \right)_{p, n_k} \cdot S + \sum_k \left(\frac{\partial H}{\partial n_k} \right)_{n_{i \neq k}, S, p} n_k = TS + \sum_{k=1}^C \mu_k n_k$$

→ Helmholtz energy

$$A \equiv U - TS = TS - pV + G - TS = G - pV$$

$$dA = TdS - p dV + \sum_k \mu_k dn_k - TdS - SdT$$

$$dA = -p dV - SdT + \sum_k \mu_k dn_k$$

$$A = A(V, T, n_k) \stackrel{\text{(Euler)}}{=} \left(\frac{\partial A}{\partial V} \right)_{T, n_k} V + \sum_k \left(\frac{\partial A}{\partial n_k} \right)_{n_{i \neq k}, V, T} n_k = -pV + \sum_k \mu_k n_k$$

→ Chemical potentials μ_k of component k in the system

$$\mu_k = \left(\frac{\partial U}{\partial n_k} \right)_{S, V, n_{i \neq k}} = \left(\frac{\partial G}{\partial n_k} \right)_{p, T, n_{i \neq k}} = \left(\frac{\partial H}{\partial n_k} \right)_{S, p, n_{i \neq k}} = \left(\frac{\partial A}{\partial n_k} \right)_{V, T, n_{i \neq k}}$$

$$G(p, T, n_k) = \sum_k \mu_k n_k$$

3 Physical meaning and relevance of TD potentials

→ Enthalpy $H = U + pV = H(S, p, n_k)$

- most important in thermochemistry

- Measurement of enthalpy changes for processes taking place under standard conditions:

The standard state of a substance at a specified T is its pure form at $p = 1 \text{ bar} = 10^5 \text{ Pa}$

physical changes like

fusion solid \rightarrow liquid

$\Delta_{\text{fus}} H^\ominus (273 \text{ K}) = +6.01 \frac{\text{kJ}}{\text{mol}}$ for water

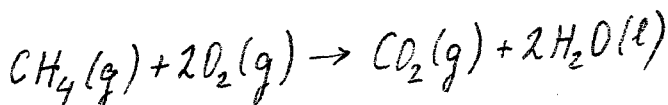
vaporization liquid \rightarrow gas

$\Delta_{\text{vap}} H^\ominus (373 \text{ K}) = +40.66 \frac{\text{kJ}}{\text{mol}}$

mixing, sublimation cf. Tables 2.3 ... 2.4 PWA p. 56, 57

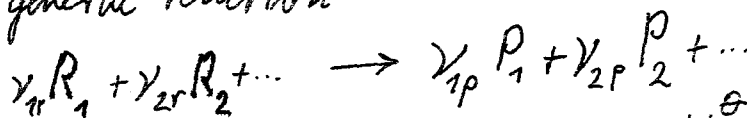
chemical changes like

combustion



$$\Delta_c H^\ominus = -890 \text{ kJ/mol}$$

general reaction



$$\Delta_r H^\ominus = \sum_{\text{products}} \nu_{kp} H_{kp}^\ominus - \sum_{\text{reactants}} \nu_{kr} H_{kr}^\ominus$$

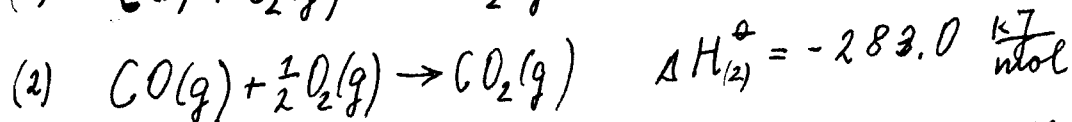
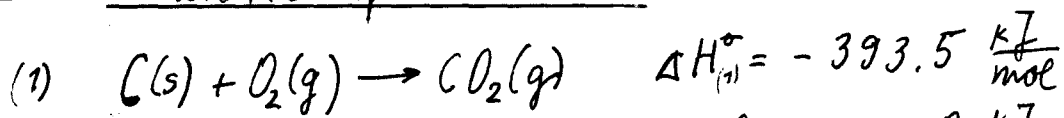
stoichiometric coefficients ν_k

standard reaction enthalpy $\Delta_r H^\ominus$

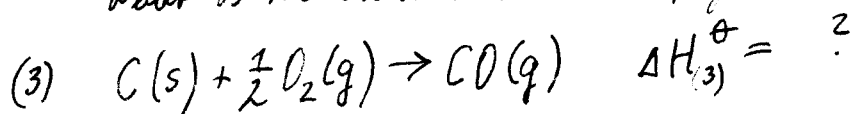
Hess's law

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction can be divided.

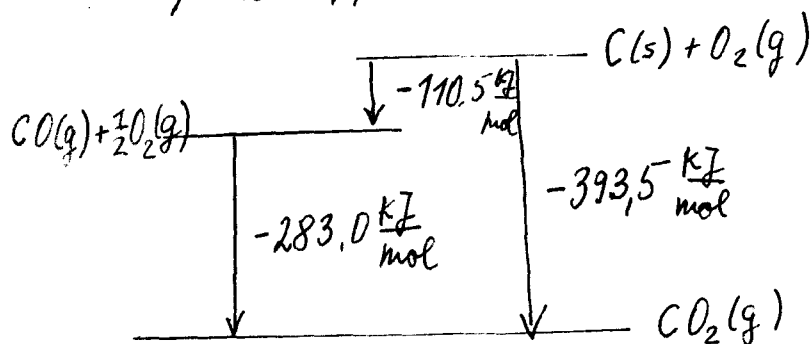
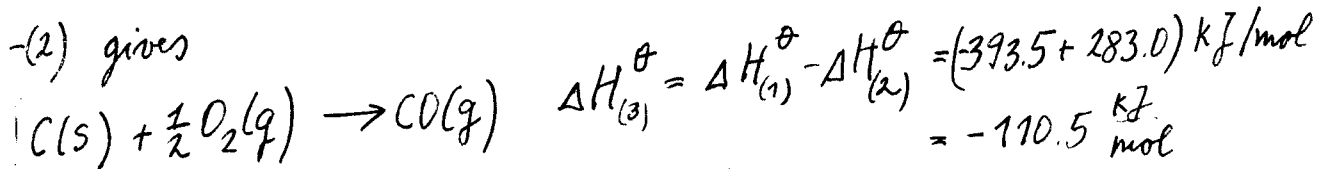
⑧ Illustration of Hess's law



— What is the standard enthalpy change for the reaction



(1) - (2) gives



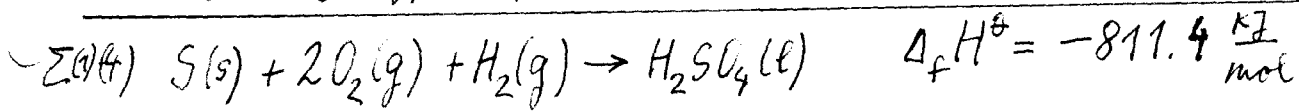
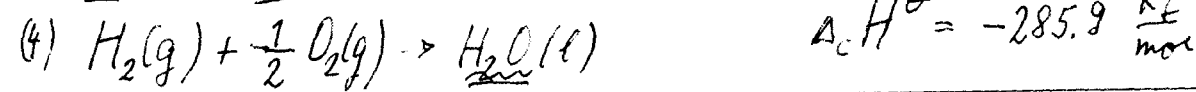
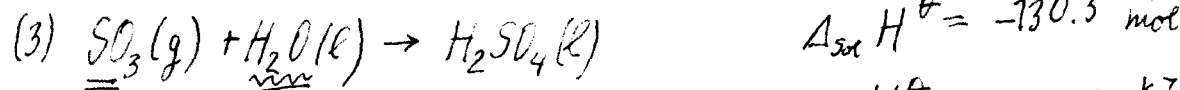
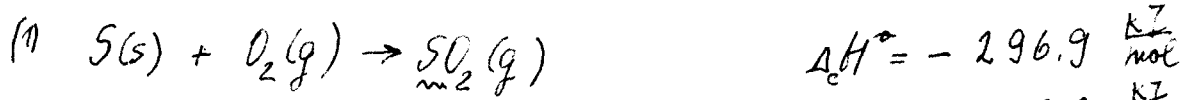
→ Standard enthalpy of formation

of a substance, $\Delta_f H^\ominus$, is the standard reaction enthalpy for the formation of the compound from its elements in their reference states (the most stable state at the specified T and $p=1 \text{ bar}$).

$$\Delta_r H^\ominus = \sum_{\text{products}} \nu_k \Delta_f H_k^\ominus - \sum_{\text{reactants}} \nu_k \Delta_f H_k^\ominus$$

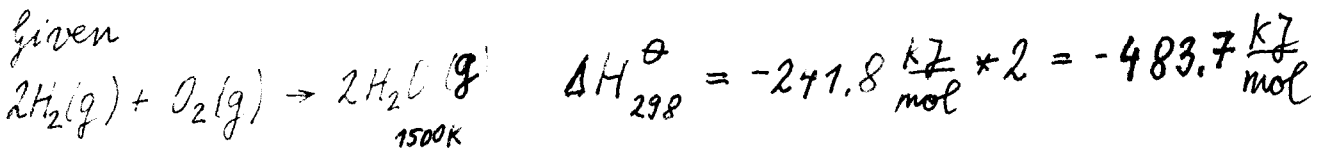
89) - Example:

→ Find the enthalpy of formation of $H_2SO_4(l)$, using the enthalpy of combustion of S to SO_2 and the enthalpy of combustion of SO_2 to SO_3 and the enthalpy of solution of SO_3 in water with the formation of H_2SO_4 .



→ Illustration of Kirchhoff's law:

Calculate the heat of combustion of H_2 at 1500K!



$$\Delta H_{1500}^\ominus = \Delta H_{298}^\ominus + \int_{298K}^{1500K} (2C_{p,H_2O} - C_{p,O_2} - 2C_{p,H_2}) dT$$

$C_p = a + bT + cT^2$ molar heat capacity at const. p

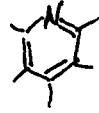
gas	$a \left(\frac{J}{mol \cdot K} \right)$	$b \cdot 10^5 \left(\frac{J}{mol \cdot K^2} \right)$	$c \cdot 10^7 \left(\frac{J}{mol \cdot K^3} \right)$	$\left(C_p \text{ in } \frac{J}{mol \cdot K} \right)$
H_2	29.07	-0.8364	20.12	
O_2	25.50	13.61	-42.56	
H_2O	30.07	9.93	8.719	

$$\Delta H_{1500}^\ominus = -483.7 + 10^{-3} \int_{298}^{1500} (-23.50 + 7.923 \cdot 10^{-3} T + 19.76 \cdot 10^{-7} T^2) dT =$$

$$= -501.1 \frac{kJ}{mol}$$

③ Note: There is no TD exact way of expressing $\Delta_f H^\ominus$ in terms of contributions from individual chemical bonds!

Kirchhoff's law



At const. pressure T_2

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

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

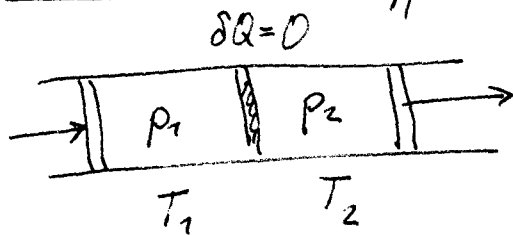
$$\rightarrow \Delta H^\ominus(T_2) = \Delta H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta C_p^\ominus dT$$

((molar quantities),
"m")

$$\Delta C_p^\ominus = \sum_{\text{products}} \nu_k C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu_k C_{p,m}^\ominus$$

((Illustration in PWA book p. 63)) example: heat of combustion of H_2 to H_2O at 1500K

Joule-Thomson-effect



example for a process of constant enthalpy

$$H_1 = U_1 + p_1 V_1 = U_2 + p_2 V_2 = H_2$$

J.-Th.-coefficient

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H = \frac{T \left(\frac{\partial V}{\partial T} \right)_p - V}{C_p} \approx \frac{\frac{2a}{RT} - b}{C_p}$$

for vd. W-gas

$$dH = T dS + V dp = \underbrace{T \left(\frac{\partial S}{\partial T} \right)_p}_{C_p} dT + \left[T \left(\frac{\partial S}{\partial p} \right)_T + V \right] dp$$

SHp
E E
VFT

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

$$T_2 \approx T_1 + \mu (p_2 - p_1)$$

for sufficiently low T
cooling \rightarrow
liquefaction of gases,
refrigerators....

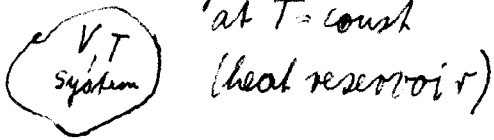
(10) Helmholtz energy

$$A \equiv U - TS = TS - pV + G - TS = G - pV$$

$$dA = -SdT - pdV + \sum_k \mu_k dn_k \quad A = A(T, V, n_k)$$

most important for processes at const. T and V

a) surroundings criterion for spontaneity



In the system are going on irreversible (spontaneous) processes, if

$$dS + dS_{env} > 0$$

$$dS_{env} = \frac{\delta Q_{env}}{T} = -\frac{dU}{T}$$

U = internal energy of the system
(Because $V = \text{const.}$ no work is done upon the system.)

$$dS + dS_{env} = dS - \frac{dU}{T} = \frac{TdS - dU}{T} = -\frac{dA}{T} > 0$$

i.e. irreversible processes in the system if $dA < 0$.

At equilibrium, A is at minimum end of lecture

b) The change in the Helmholtz energy is equal to the maximum work accompanying the process: $\delta W_{max} = \Delta A$

Proof: $\delta W = dU - \delta Q$ (1. law) $\delta Q \leq TdS$ (2. law)

$$\delta W_{max} = dU - TdS = dA \quad (\text{for isothermal processes})$$

A = "maximum work function" or "free energy" (energy for work)

(11) Gibbs energy

$$G \equiv H - TS$$

$$dG = -SdT + Vdp + \sum_k \mu_k dn_k \quad G = G(p, T, n_k)$$

most important for processes at const. p and T

a) Criterion for spontaneous reactions (at const. p and T)

$$dS + dS_{\text{env}} > 0$$

$$dS_{\text{env}} = \frac{\delta Q_{\text{env}}}{T} = -\frac{dH}{T} \quad \leftarrow \text{enthalpy change of the system (at } p = \text{const.)}$$

$$dS - \frac{dH}{T} = -\frac{dH - TdS}{T} = -\frac{dG}{T} > 0$$

$dG < 0$ irreversible (spontaneous) process

At equilibrium, G is at a minimum.

b) Maximum non-expansion work $\delta W_{\text{add, max}}$

At const. T and p , the maximum additional (non-expansion) work, is given by dG

Proof: $H = U + pV \quad dH = \delta Q + \delta W + d(pV)$

$$dG = dH - TdS - SdT = \delta Q + \delta W + d(pV) - TdS - SdT$$

$dT = 0$ (isoth. change)

When the change is reversible $\delta W = \delta W_{\text{rev}}$ and $\delta Q = TdS$,

i.e. for a reversible isothermal process

$$dG = \delta W_{\text{rev}} + d(pV) = -pdV + \delta W_{\text{add, rev}} + pdV + Vdp$$

$$dG = \delta W_{\text{add, rev}}$$

i.e. $dG = \delta W_{\text{add, rev}} = \delta W_{\text{add, max}}$

(12)

c) ΔG and ΔH as criterion for equilibrium

At $T = \text{const}$ we have for the changes of G and H

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta U - T\Delta S$$

spontaneous process for $\Delta G < 0$, which is favored for

$$\underbrace{\Delta H < 0}_{\text{decrease of energy}} \quad \text{or/and} \quad \underbrace{\Delta S > 0}_{\text{increase of disorder}}$$

decrease of energy

increase of disorder

$\approx | \Delta H | \gg | T\Delta S |$ "enthalpy controlled process"

$| \Delta H | \ll | T\Delta S |$ "entropy controlled process"
(mostly at high temperatures)

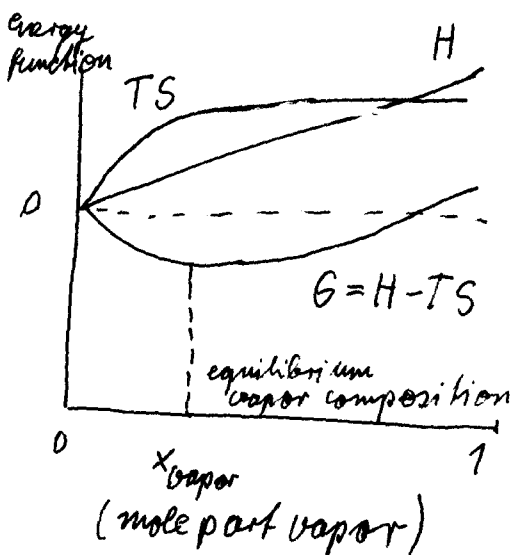
Illustration

evaporation of a solid in a closed space
"sublimation"

solid $\hat{=}$ low H, U ; low S

vapor $\hat{=}$ higher H, U ; higher S

\rightarrow dominance of $\Delta H, U$ would lead to complete condensation
" " $T\Delta S$ " " " " " evaporation



13) Third Law

$$\lim_{T \rightarrow 0} S(V, T) = 0$$

$$\lim_{T \rightarrow 0} S(p, T) = 0$$

$$\rightarrow \begin{cases} C_p = T \left(\frac{\partial S}{\partial T} \right)_p \rightarrow 0 \\ C_v = T \left(\frac{\partial S}{\partial T} \right)_V \rightarrow 0 \end{cases} \quad \left\{ \begin{array}{l} \text{heat capacities} \end{array} \right.$$

$$\rightarrow \left\{ S = \frac{U - F}{T} \rightarrow 0 \right. \quad T \rightarrow 0$$

$$\rightarrow \left\{ \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow 0 \right. \quad \left\{ \begin{array}{l} \text{isobaric} \\ \text{expansion} \\ \text{coefficient} \end{array} \right.$$

because $\left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0$

SHP
EG
VFT

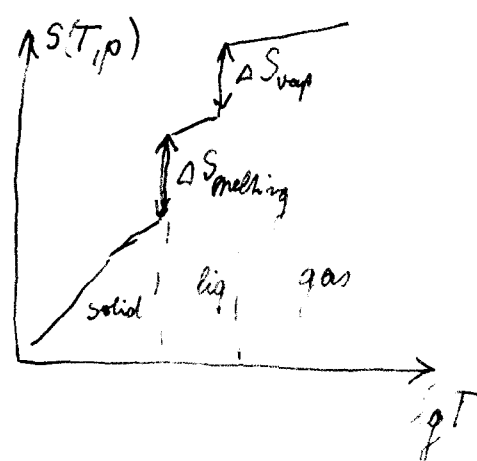
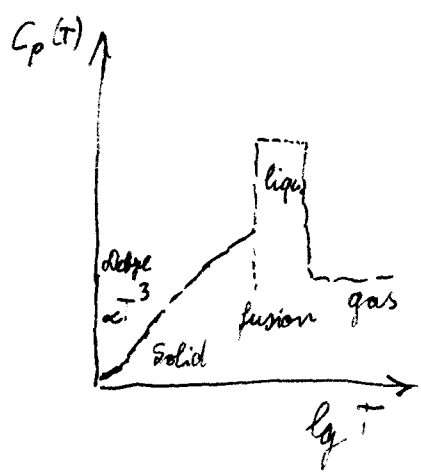
applications

→ 0, absolute values of entropy

$$S(T, p) = S(0, p) + \int_0^{T_{t_1}} \frac{C_p(T)}{T} dT + \frac{\Delta H_{t_1}}{T_{t_1}} + \int_{T_{t_1}}^{T_{t_2}} \frac{C_p(T)}{T} dT + \frac{\Delta H_{t_2}}{T_{t_2}}$$

(3. law)

T_{t_1} = temperature of 1st phase transition
 ΔH_{t_1} = transition enthalpy

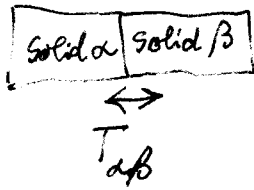


Debye: $C_p = \text{const. } T^3$

PWA Table 2.5 absolute values of standard molar entropies S_m^\ominus

14

→ b) transition entropies of allotropic solids { several forms of structure which are stable in diff. T-ranges



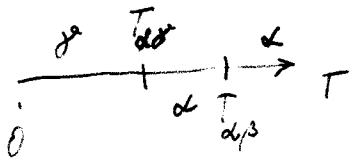
$$\Delta S_{\alpha\beta} = S_{\alpha} - S_{\beta} = \int_0^{T_{\alpha\beta}} \frac{C_{p\alpha}}{T} dT - \int_0^{T_{\alpha\beta}} \frac{C_{p\beta}}{T} dT \stackrel{Z}{=} \frac{\Delta H_{\alpha\beta}}{T_{\alpha\beta}}$$

Independent measurements of $\Delta H_{\alpha\beta}$, $T_{\alpha\beta}$ and $C_{p\alpha}(T)$, $C_{p\beta}(T)$
 graphite \leftrightarrow diamond

→ Numerical example PH_3

$T_{\alpha\beta} = 49.43 \text{ K}$

two crystalline forms α , β



α -form \rightarrow δ -crystal at $T_{\delta} = 30.29 \text{ K}$

S_{β}	$J / (\text{mol K})$
0...15K (debye)	1.414
15...49.43K	16.91
Σ	18.32

S_{α}	$J / (\text{mol K})$
0...15K (δ -form)	2.071
15...30.25	9.142
$\Delta S_{\delta \rightarrow \alpha}$	2.707
30.29...49.43	20.083
Σ	34.003

At $T_{\alpha\beta}$ $\Delta S_{\alpha\beta} = (34.003 - 18.32) \frac{J}{\text{mol K}} = 15.683 \frac{J}{\text{mol K}}$

Directly measured $\Delta S_{\alpha\beta}$ (via $\Delta H_{\alpha\beta} = T_{\alpha\beta} \Delta S_{\alpha\beta}$) gives $\Delta S_{\alpha\beta} = 15.72 \frac{J}{\text{mol K}}$

15) c) Reaching very low temperatures
adiabatic demagnetization

