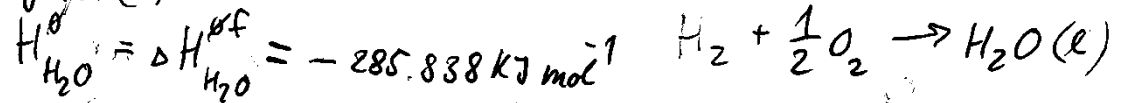


# Termodynamika a fázové vlastnosti jednosložkových soustavy



# Výpočet Td funkcí vody

Výp. stand. hodnot  $H^\ominus, S^\ominus, G^\ominus$  (1 mol  $H_2O$  v soustavě)  
 Liguíd (l):



$$S_{H_2O}^\ominus = S_{H_2}^{\ominus f} + \left( S_{H_2}^\ominus + \frac{1}{2} S_{O_2}^\ominus \right) = -163,292 \text{ J mol}^{-1} \text{ K}^{-1}$$

TAB:  $\Delta S_{H_2O}^\ominus = -163,292 \text{ J mol}^{-1} \text{ K}^{-1}$   
 $S_{H_2}^\ominus = 130,587$  —  
 $S_{O_2}^\ominus = 205,29$  —

$$G_{H_2O}^\ominus = H_{H_2O}^\ominus - T \cdot S_{H_2O}^\ominus = -306,690 \text{ kJ mol}^{-1}$$

Výpočet pro jinou  $T = 373 \text{ K}$   $C_p^m = 75,383 \text{ J K}^{-1} \text{ mol}^{-1}$

$$H(T) = H^\ominus + \int_{T^\ominus}^T C_p^m dT = H^\ominus + C_p^m \cdot (T - T^\ominus) = -280,184 \text{ J mol}^{-1}$$

$$S(T) = S^\ominus + \int_{T^\ominus}^T \frac{C_p^m}{T} dT = S^\ominus + C_p^m \cdot \ln \frac{T}{T^\ominus} = 86,82 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$G(T) = H(T) - T \cdot S(T) = -312,594 \text{ J mol}^{-1}$$

Výpočet pro tlak  $p = 50 \text{ Atm}$

$$(V_m = 18 \text{ cm}^3)$$

$$G_2(p) = G(p_0) + V_m \cdot (p - p_0) =$$

$$= -312,594 + 18 \cdot 10^{-6} \cdot (50 - 1) \cdot 101,325 = -312,505 \text{ J mol}^{-1}$$

# Fázový přechod

TAB: 1 Atm:

T [K]	$\Delta H_{\text{vap}}$ [kJ mol <sup>-1</sup> ]
298	44.01
373	40.67

$$H_{H_2O}^g(373K) = H^l(373) + \Delta H_{\text{vap}}(373, 1 \text{ Atm}) = -280184 + 40.69 \cdot 10^3 =$$

$$= \underline{\underline{-239914 \text{ J mol}^{-1}}}$$

$$S^g(373) = S^l(373) + \frac{\Delta H_{\text{vap}}}{T_v} = 86.85 + \frac{40670}{373} = \underline{\underline{195.88 \text{ J mol}^{-1} \text{ K}^{-1}}}$$

$$G^g(373) = H^g(373) - T_v \cdot S^g(373) = \underline{\underline{-312594 \text{ J mol}^{-1}}} = G^l(373)$$

Plynový stav:  $T = 473K$ ,  $p = 1 \text{ Atm}$ ,  $\text{H}_2\text{O}(\text{gas})$   $p_v(373-500K)$

$$H^g(T) = H^g(373) + \int_{T_v}^T c_p dT = \quad \text{TAB: } c_p^m(g) = 30.12 + 11.30 \cdot T$$

[J mol<sup>-1</sup> K<sup>-1</sup>]

$$= H^g(373) + \int_{T_v}^T (a + b \cdot T) dT = H^g(373) + a \cdot (T - T_v) + \frac{b}{2} (T^2 - T_v^2) =$$

$$= \underline{\underline{241657 \text{ J mol}^{-1}}}$$

$$S^g(T) = S^g(373) + \int_{T_v}^T \frac{c_p}{T} dT = S^g(373) + \int_{T_v}^T \frac{(a + b \cdot T)}{T} dT =$$

$$= S^g(373) + a \cdot \ln \frac{T}{T_v} + b \cdot (T - T_v) = \underline{\underline{1332.997 \text{ J mol}^{-1} \text{ K}^{-1}}}$$

$$G^g(T) = H^g - T \cdot S^g = \underline{\underline{-389050 \text{ J mol}^{-1}}}$$

$T = 473K$ ,  $p = 50 \text{ Atm}$ ,  $\text{id. gas}$

$$G(p) = G(p_0) + RT \ln \frac{p_0}{p} = -389050 + 8.314 \cdot 473 \cdot \ln \frac{50}{1} =$$

$$= \underline{\underline{-373661 \text{ J mol}^{-1}}}$$

1 Atm

List5

50 Atm

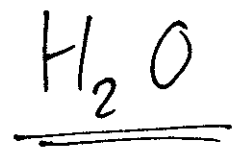
G(liquid)-G(gas)

T [K]	101325	1094310	2087295	3080280	4073265	5066250
298,15	23240,29	17359,36	15776,46	14829,64	14154,83	13631,91
306,8925	17294,57	11240,52	9610,641	8635,512	7940,374	7401,576
315,635	12202,74	5975,58	4298,718	3295,277	2579,811	2025,142
324,3775	7965,122	1564,843	-158,998	-1190,75	-1926,55	-2497,09
333,12	4582,002	-1991,39	-3762,21	-4822,28	-5578,4	-6164,81
341,8625	2053,664	-4692,85	-6510,65	-7599,02	-8375,47	-8977,76
350,605	380,3713	-6539,26	-8404,03	-9520,72	-10317,5	-10935,7
359,3475	-437,623	-7530,37	-9442,12	-10587,1	-11404,2	-12038,3
368,09	-400,078	-7665,94	-9624,67	-10798	-11635,4	-12285,3
376,8325	493,2325	-6945,74	-8951,46	-10153,1	-11010,8	-11676,6
385,575	2242,528	-5369,56	-7422,26	-8652,19	-9530,29	-10211,9
394,3175	4848,015	-2937,19	-5036,87	-6295,11	-7193,53	-7891,04
403,06	8309,893	351,5698	-1795,08	-3081,64	-4000,39	-4713,77
411,8025	12628,35	4496,913	2303,282	988,415	49,33443	-679,918
420,545	17803,57	9499,019	7258,409	5915,231	4955,822	4210,698
429,2875	23835,73	15358,06	13070,47	11698,98	10719,25	9958,251
438,03	30725	22074,21	19739,64	18339,84	17339,78	16562,91
446,7725	38471,53	29647,63	27266,08	25837,97	24817,57	24024,83
455,515	47075,48	38078,46	35649,93	34193,51	33152,78	32344,18
464,2575	56537	47366,86	44891,36	43406,62	42345,57	41521,09
473	66856,23	57512,97	54990,49	53477,44	52396,06	51555,71

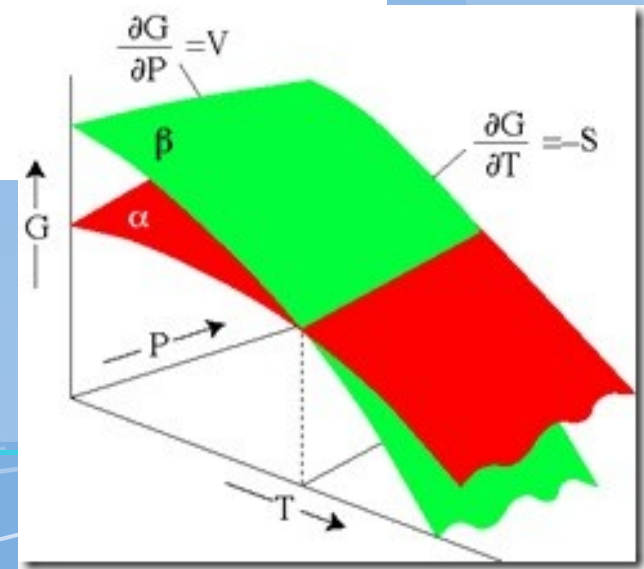
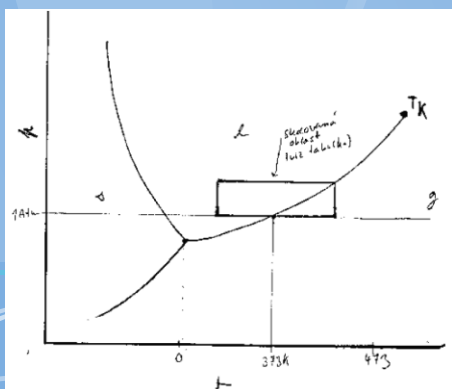
373K = 100°C

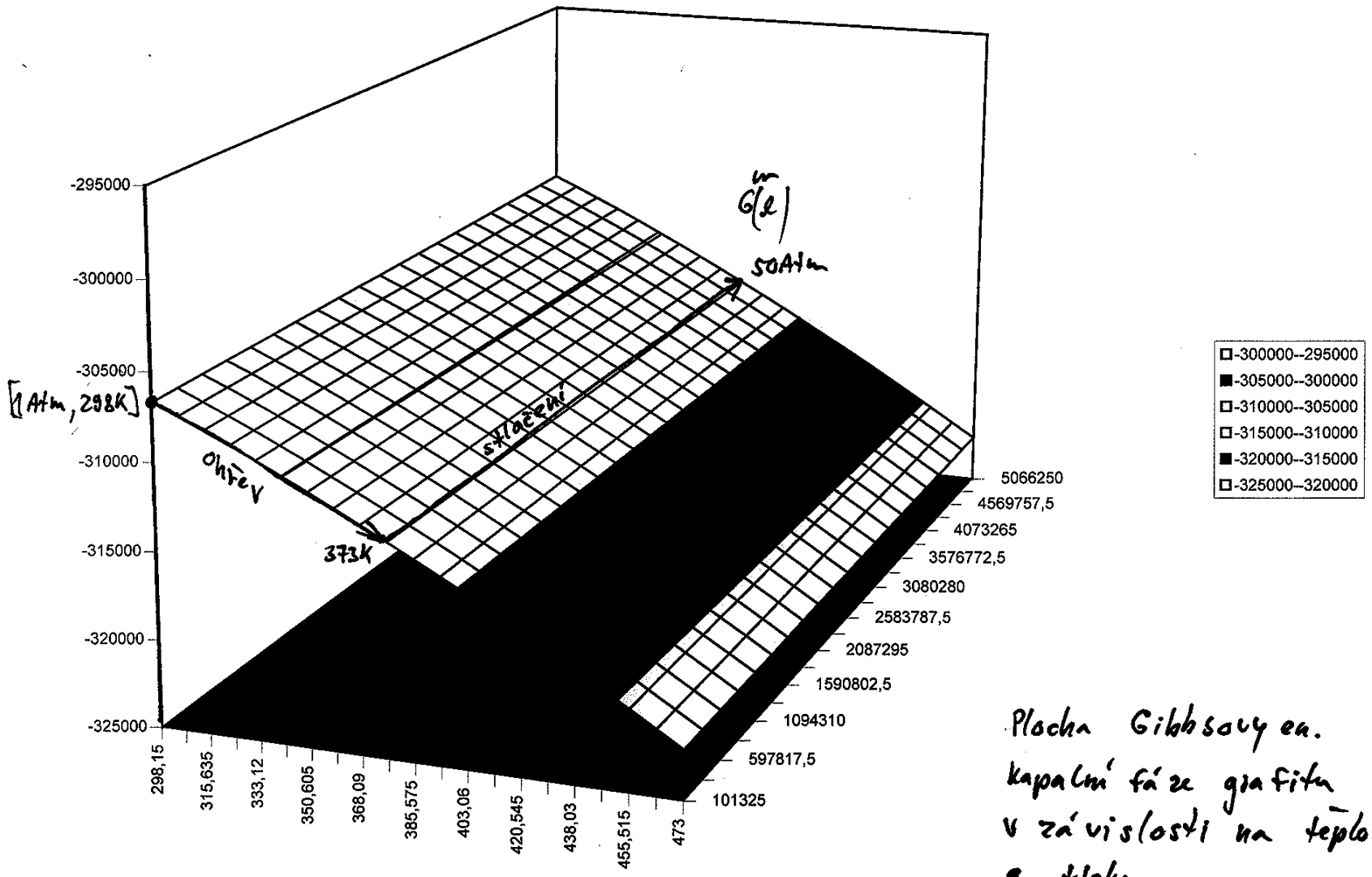
meno  
indevac  
přetvořiti  
C<sub>p</sub>

výpočet  
hranice fázových  
oblastí l-g  
pro soustavu



(l→g)  
hranice veče  
přibližně zde

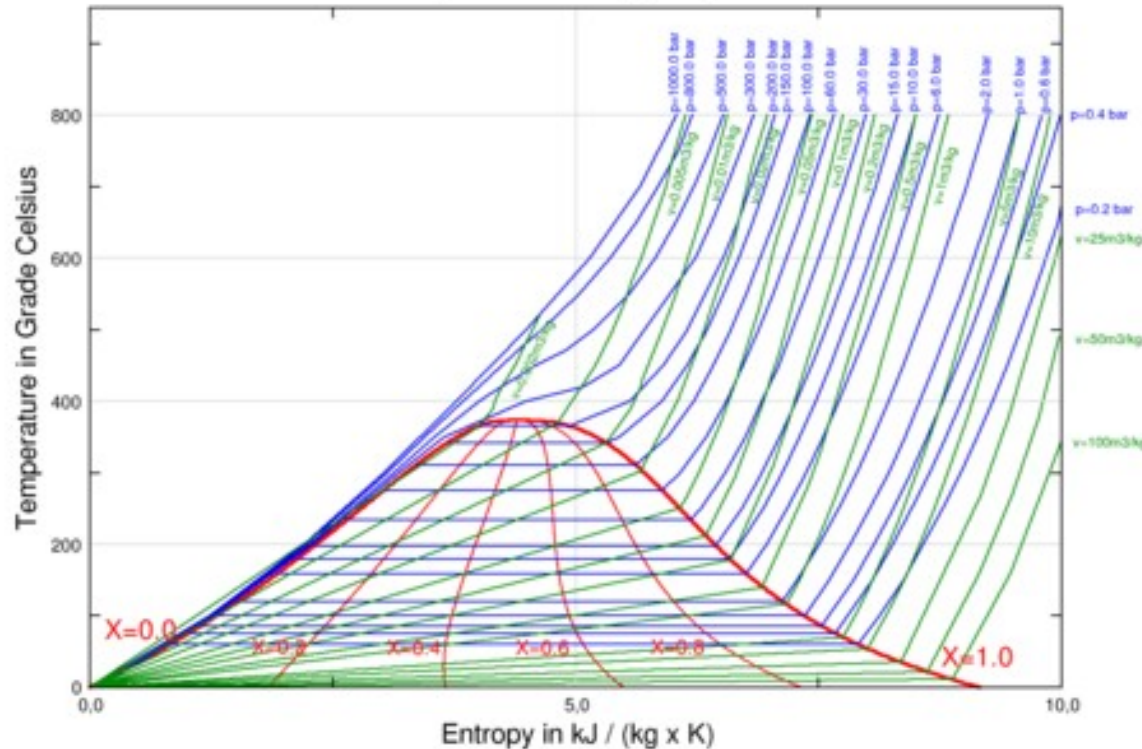




Plocha Gibbsovy en.  
 kapalní fáze grafitu  
 v závislosti na teplotě  
 a tlaku

Fázové diagramy a termodynamické funkce různých kapalin:  
<http://fluidproperties.blogspot.cz/>

Water Steam  
Temperature-Entropy-Diagram



Temperature vs. specific entropy phase diagram for water/steam. In the area under the red dome, liquid water and steam coexist in equilibrium. The critical point is at the top of the dome. Liquid water is to the left of the dome. Steam is to the right of the dome. The blue lines/curves are **isobars** showing constant pressure. The green lines/curves are **isochores** showing constant specific volume. The red curves show constant quality.

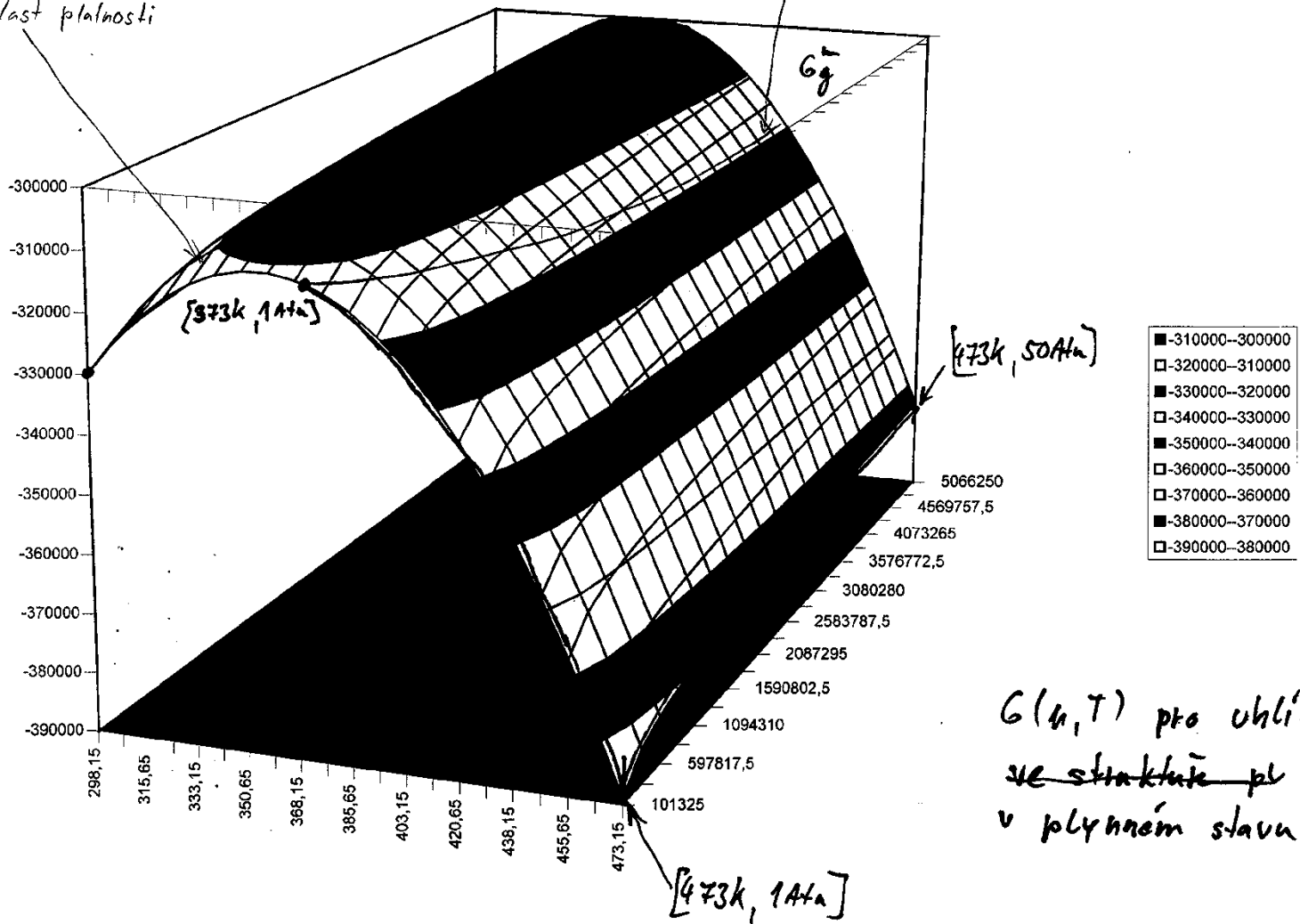
Read more: <http://www.answers.com/topic/phase-diagram#ixzz2fheybptD>



gas graf 2

průsečnice křivek  $G_D^m$  a  $G_D^n$

$C_p^h$  mimo oblast platnosti



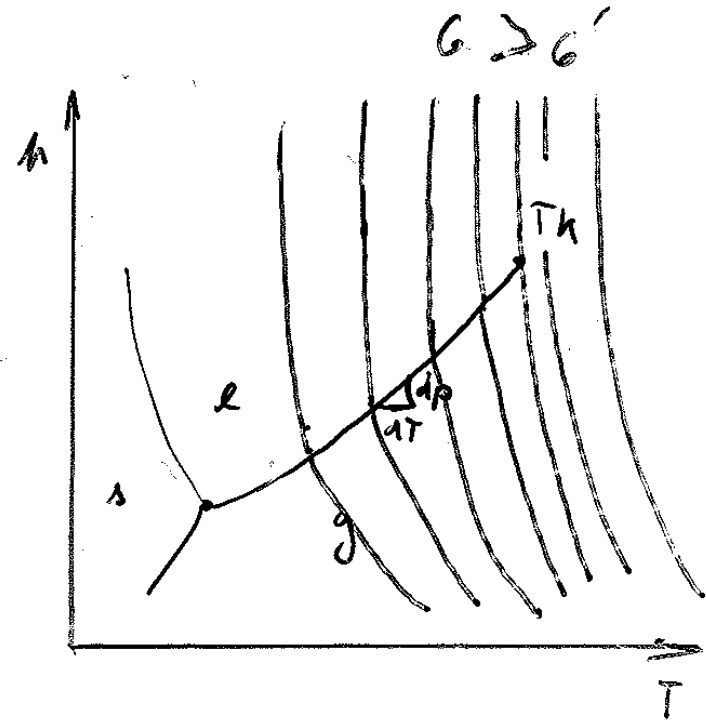
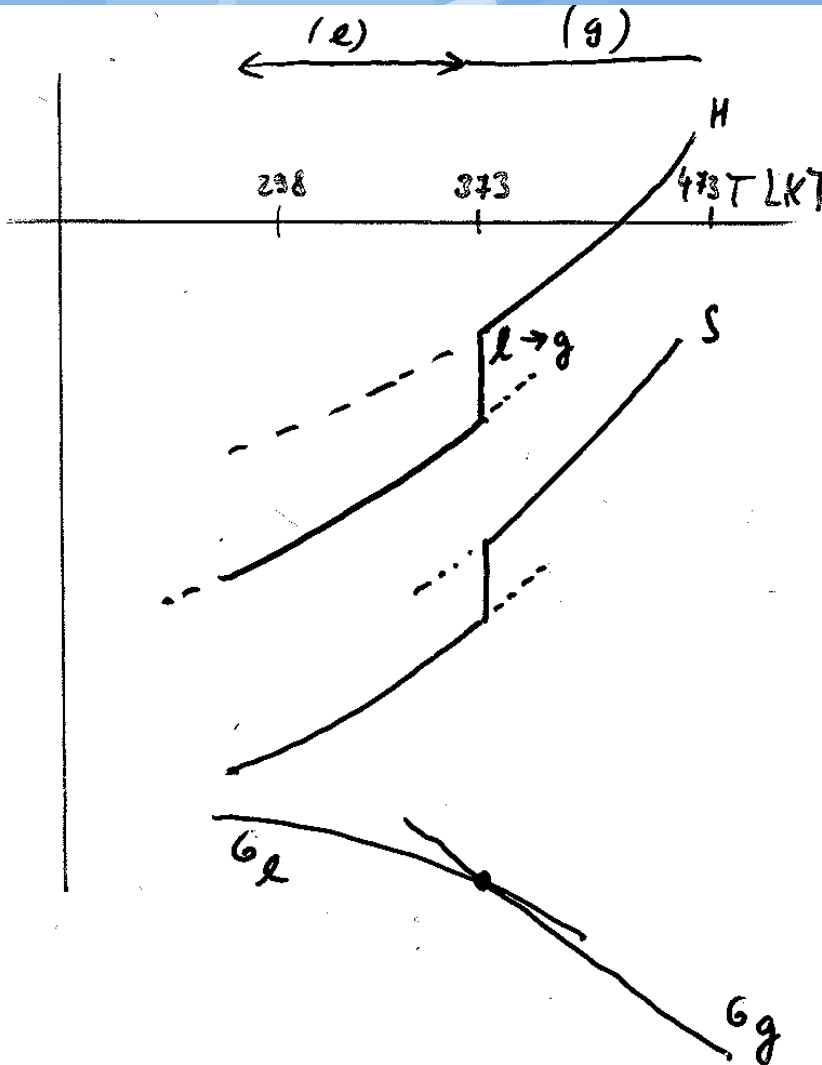
$G(u, T)$  pro uhlík  
ze struktury pl  
v plynném stavu

## Závěry k příkladu H<sub>2</sub>O (platí obecně)

- ① z experimentální Luich termod. dat lze spočítat termod. data  $H, S, G$  pro všechny fáze  $s, l, g$
- ② pro dané  $T, p$  je stabilní fáze s nejnižší hodnotou  $G$  za těchto podmínek  $T$  a  $p$
- ③ průsečnickové křivky ploch  $G^s, G^l, G^g$  udávají v souřadnicích  $p$  a  $T$  hranice fázových oblastí ve fáz. diagramu
- ④ v oblasti nad kritickým bodem plochy  $G^l$  a  $G^g$  splývají v jednu
- ⑤ hodnoty  $G$  jsou velké ale málo se liší  $\rightarrow$  \*  
hutnost přesnosti výchozích dat ( $C_p, \Delta H_{f_1 \rightarrow f_2}, S^0, \dots$ )
- ⑥ Je třeba sledovat interval platnosti exp. fázových dat  $\Delta H_{f_1 \rightarrow f_2}, C_p$  (pozor na  $\Delta H_{vap}$ ).

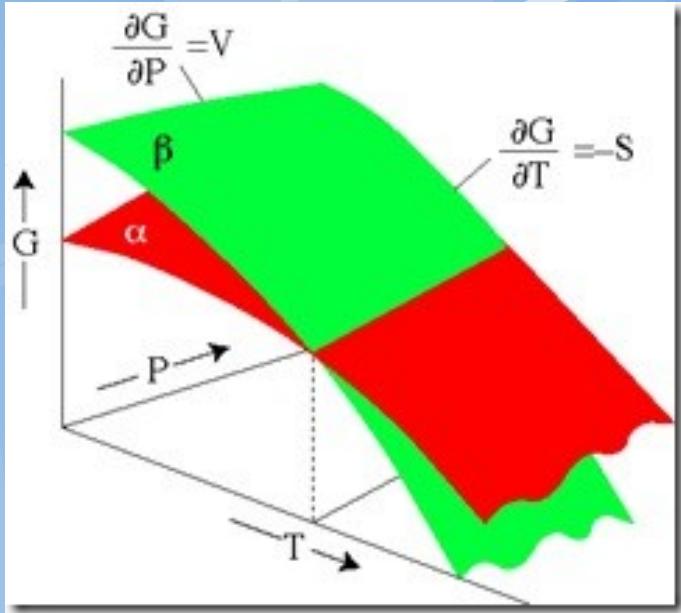


# Text konzistence TD dat



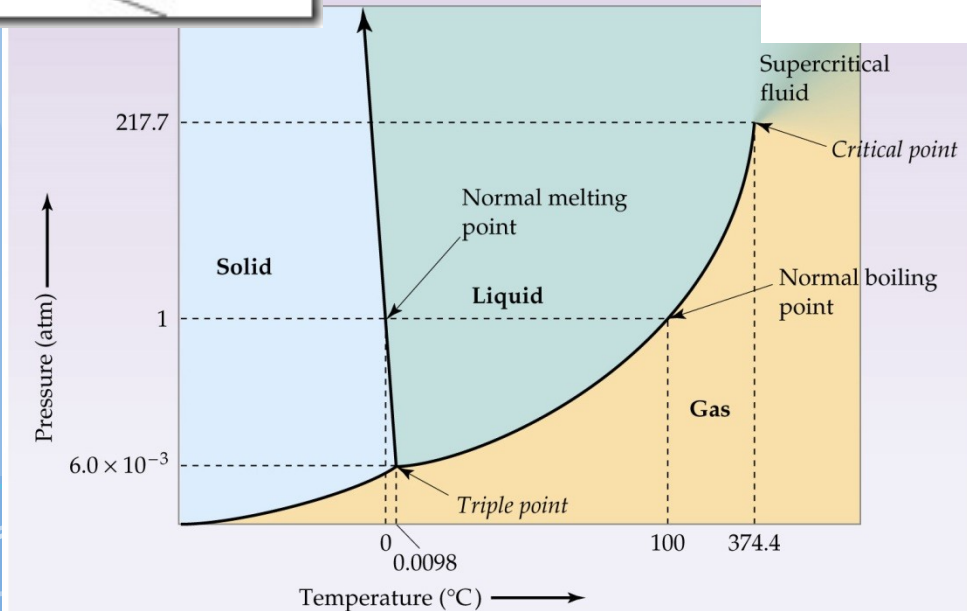
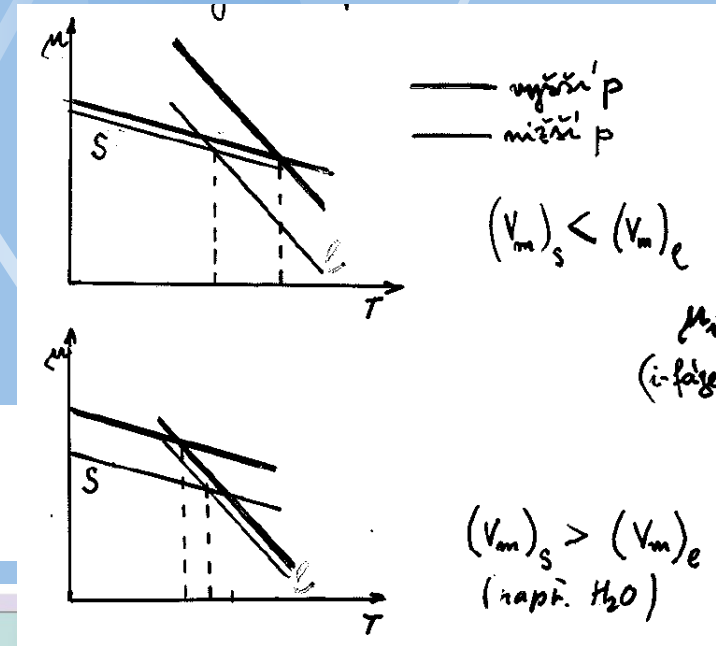
- ⊗ pozor pokud kombinujeme f-a pro různé fáze
- ∇ Test konzistence

# Jednosložkové fázové diagramy



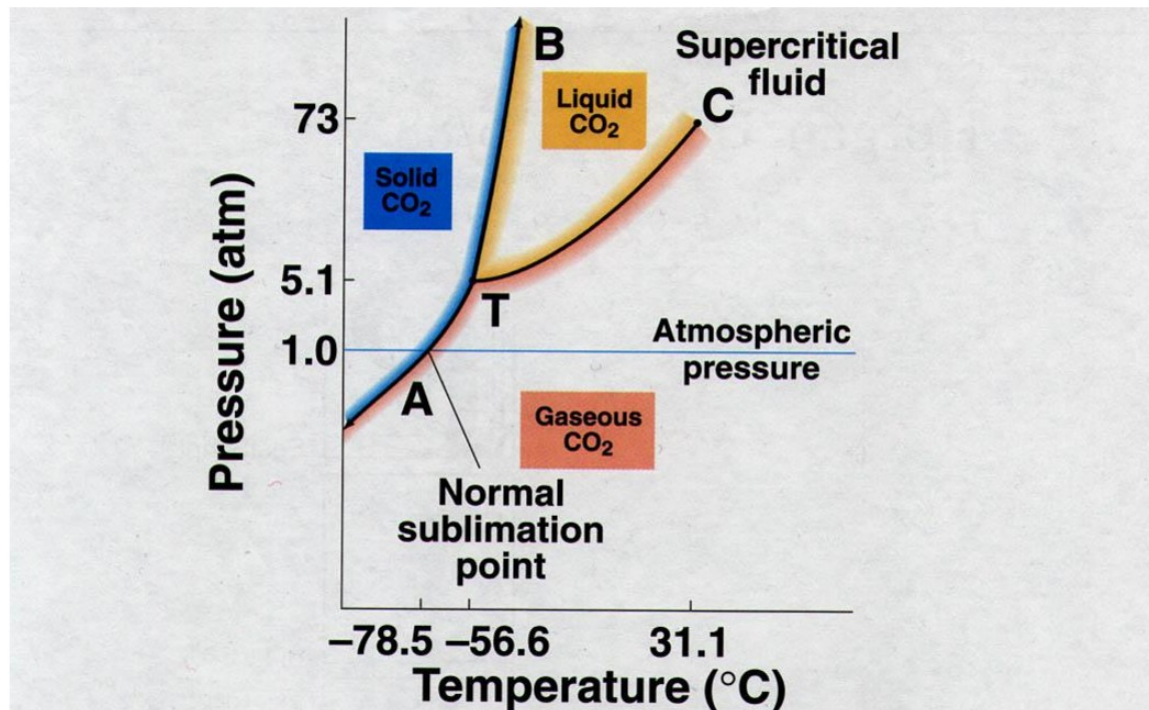
● H<sub>2</sub>O

za rovnováhy  
platí  $\mu_{\alpha}^i = \mu_{\beta}^i$

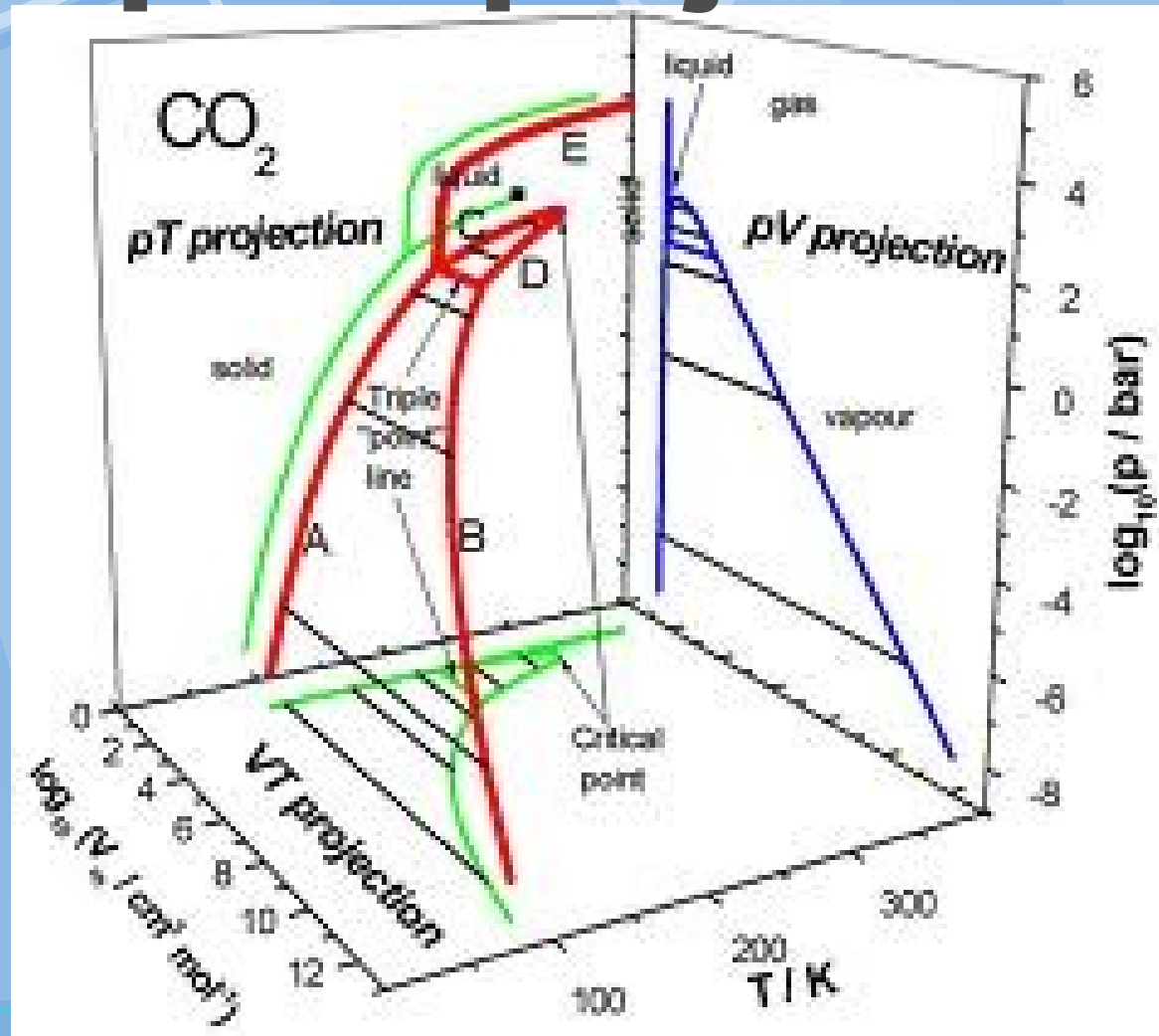


# CO<sub>2</sub>

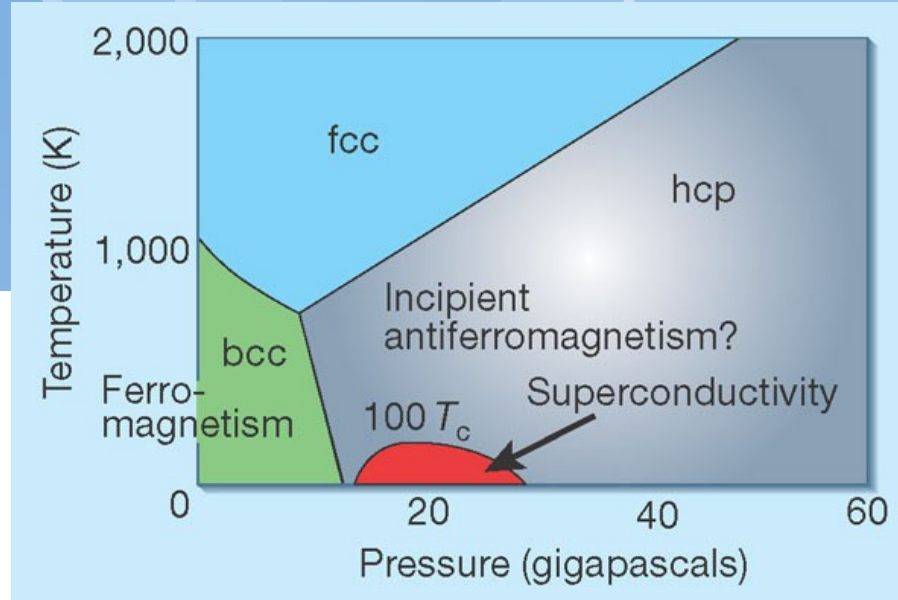
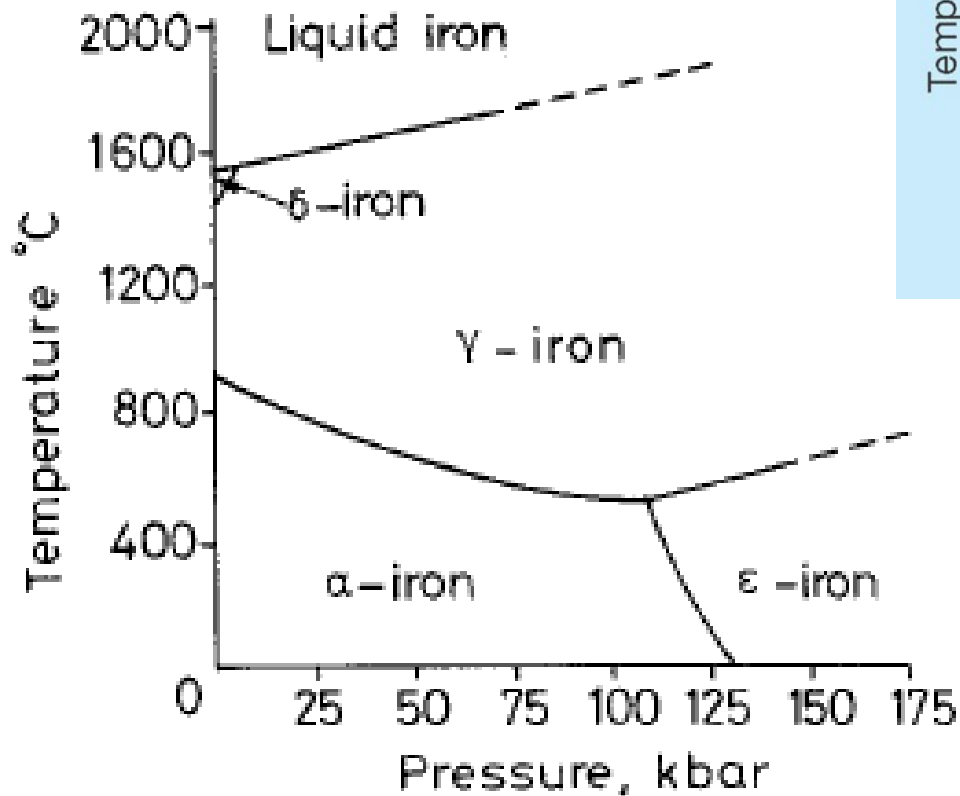
## Phase Diagram for CO<sub>2</sub>



# T-p-Vm projekce

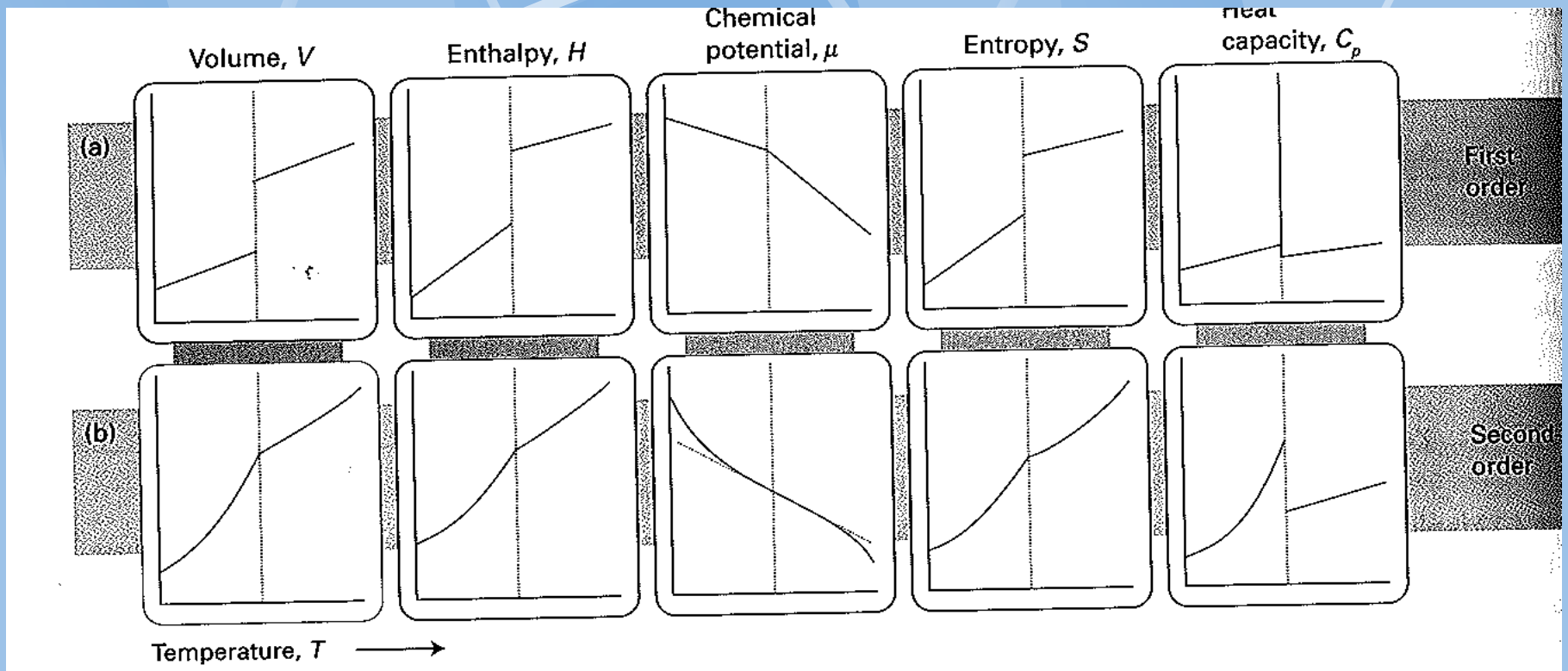


# FD železa



Predikce fází

# Klasifikace fázových přechodů



TD Kritérium:

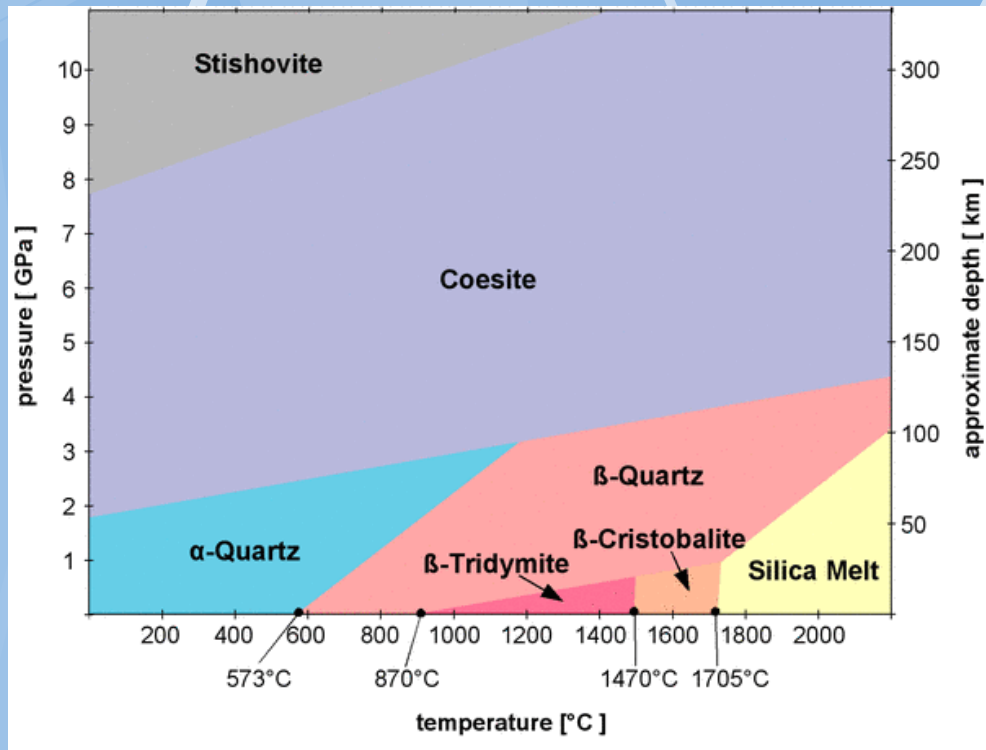
$$\left( \frac{\partial \mu(\beta)}{\partial p} \right)_T - \left( \frac{\partial \mu(\alpha)}{\partial p} \right)_T = V_m(\beta) - V_m(\alpha) = \Delta_{\text{trs}} V$$

$$\left( \frac{\partial \mu(\beta)}{\partial T} \right)_p - \left( \frac{\partial \mu(\alpha)}{\partial T} \right)_p = -S_m(\beta) + S_m(\alpha) = -\Delta_{\text{trs}} S = -\frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$



# Příklady řechodů 1. druhu

Přemístění složek, atomů, iontů, atd.



SiO<sub>2</sub>

Galium  
 $T_m = 29,7645^\circ$   
C, (302,9145 K)

# Pravidla pro změny entropie fázových přechodů

Troutonovo pravidlo:

$$\Delta S_{\text{vapn}}^{\circ} = \frac{\Delta H_{\text{vapn}}^{\circ}}{T_{\text{bp}}} \approx 87 \text{ J/mol} \cdot \text{K}$$

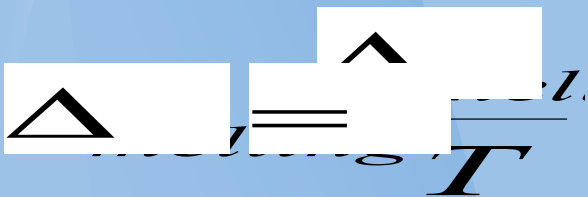


Richardsovo pravidlo:

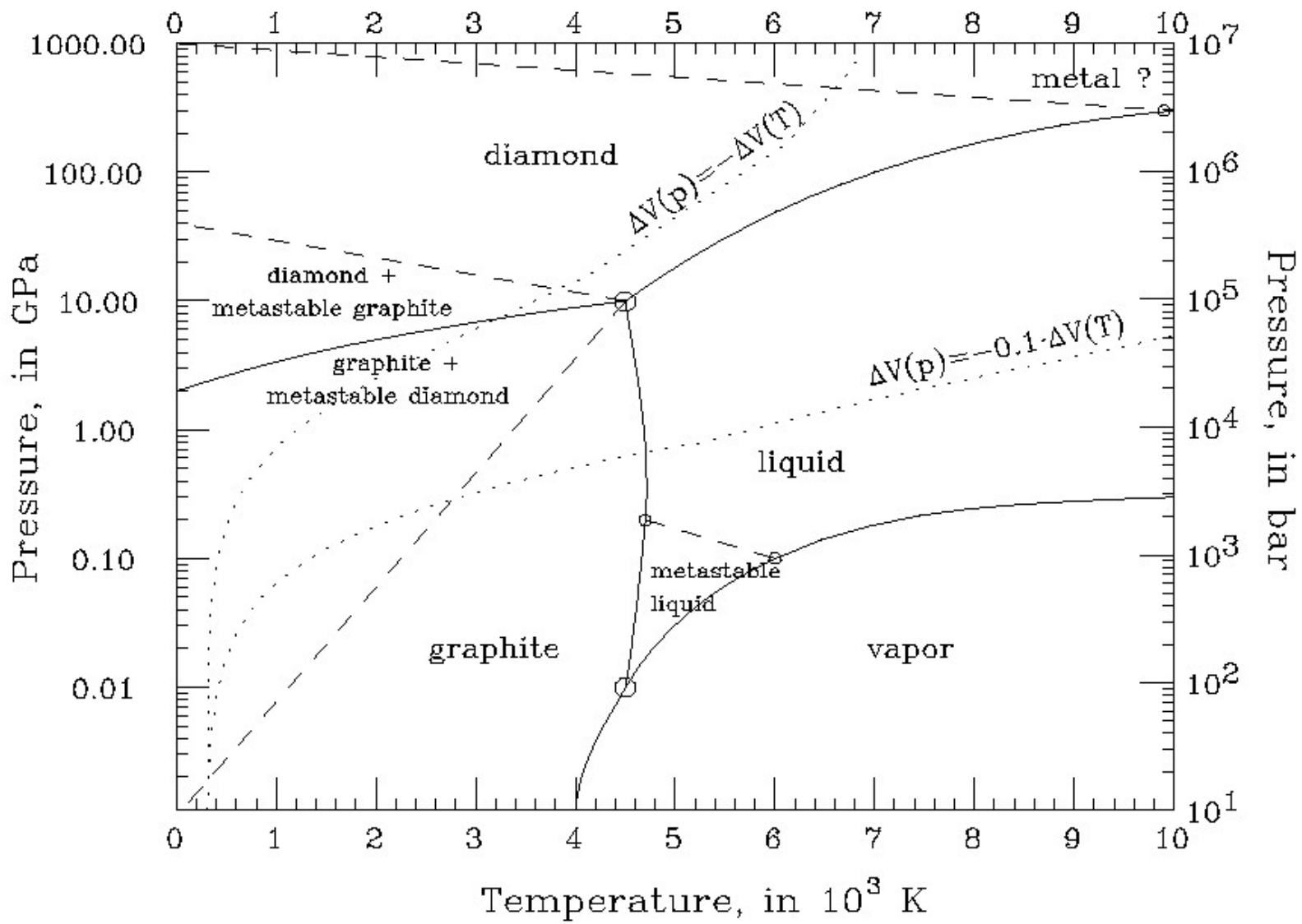
9.2 J/mol....prvky s kovovou vazbou

21-29 J/mol.... anorganické sloučeniny

37-59 J/mol .....nízkomolekulární organické látky



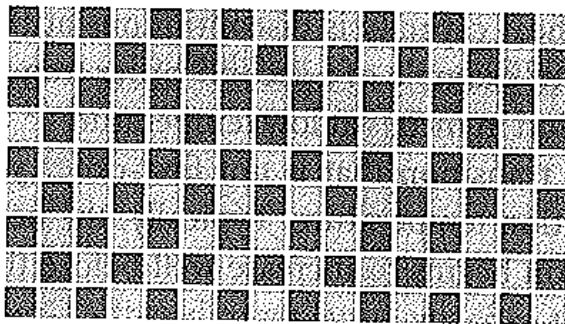
# Uhlík



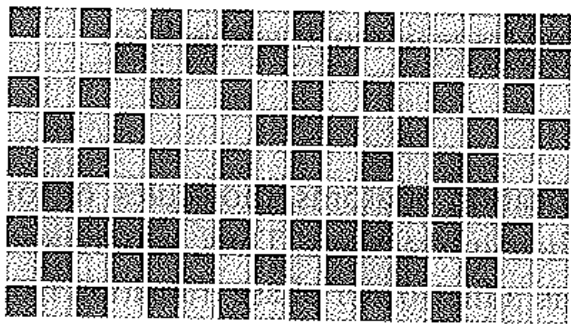
# Příklady přeměn 2 druhu

Změny symetrie

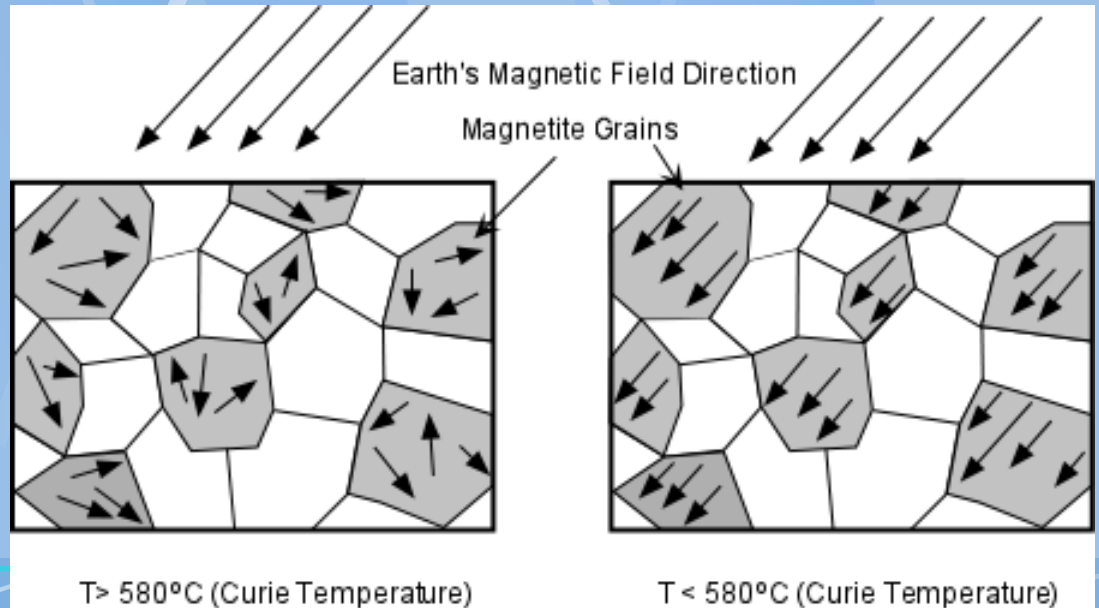
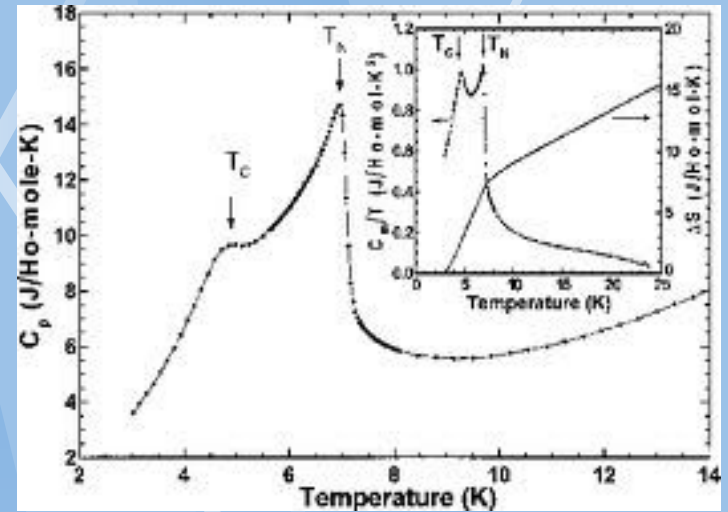
Uspořádací přeměny



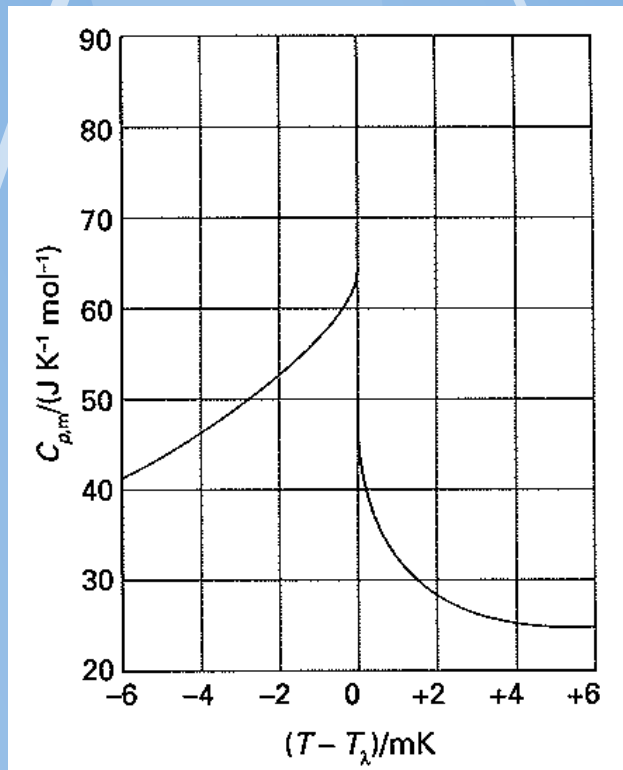
(a)



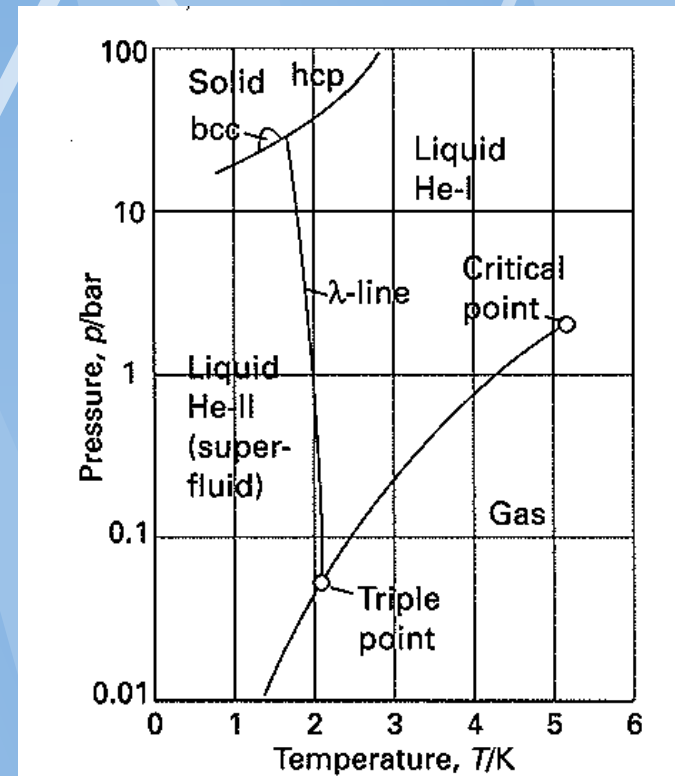
(b)



# Supravodivost He



The  $\lambda$ -curve for helium,



Supravodivá oblast helia

# Clausius clapeyronova rovnice

## Obecné odvození Clausius-Clapeyronovy r-ice

Taylorův rozvoj

Na ploše  $G^g(T, p)$ :

$$G(T, p)^g = \mu^g = G^g(T_0, p_0) + \left( \frac{\partial G^g}{\partial p} \right)_T dp' + \left( \frac{\partial G^g}{\partial T} \right)_p dT' + \dots$$

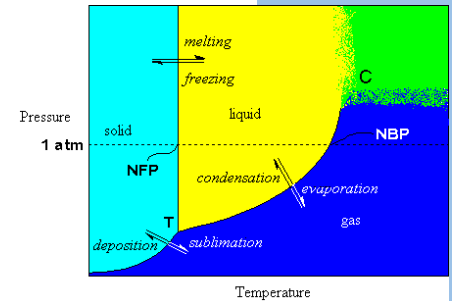
Na ploše  $G^l(T, p)$ :

$$G(T, p)^l = \mu^l = G^l(T_0, p_0) + \left( \frac{\partial G^l}{\partial p} \right)_T dp'' + \left( \frac{\partial G^l}{\partial T} \right)_p dT'' + \dots \quad (14)$$

Jestliže  $[T_0, p_0]$  leží na průnikové křivce  $G^l$  a  $G^g$  a nový bod  $[T, p]$  leží také na ní, platí:

$$G^g(T, p) = G^l(T, p); \quad G^g(T_0, p_0) = G^l(T_0, p_0); \quad \underbrace{dp'}_{=dp} = \underbrace{dp''}, \quad \underbrace{dT'}_{=dT} = \underbrace{dT''}$$

Další (12)-(14) dle:





Pak (13)-(14) dá:

$$\left(\frac{\partial G^g}{\partial p}\right)_T dp + \left(\frac{\partial G^g}{\partial T}\right)_p dT = \left(\frac{\partial G^l}{\partial T}\right)_p dt + \left(\frac{\partial G^l}{\partial p}\right)_T dT$$

= dp                      = dT

oběma C.C. + ce

po úpravách

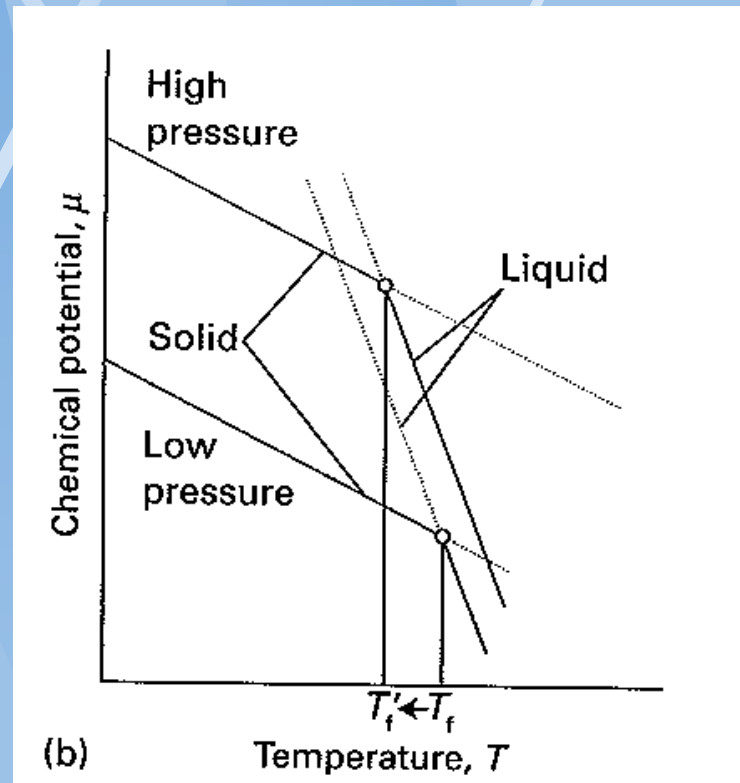
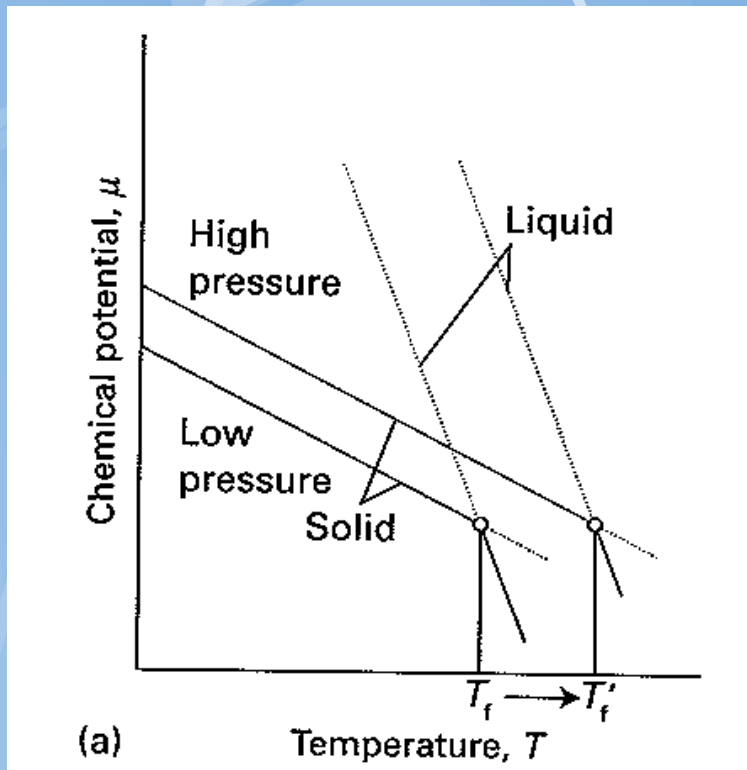
$$\boxed{\frac{dp}{dT} = \frac{\left(\frac{\partial G^g}{\partial T}\right)_p - \left(\frac{\partial G^l}{\partial T}\right)_p}{\left(\frac{\partial G^g}{\partial p}\right)_T - \left(\frac{\partial G^l}{\partial p}\right)_T} = \frac{s^g - s^l}{v^g - v^l} = \frac{\Delta S_m^{g \rightarrow l}}{\Delta V_m^{g \rightarrow l}} = \frac{\Delta H_m^{g \rightarrow l}}{T \Delta V_m^{g \rightarrow l}}}$$

plati' obecně pro jakýkoliv fázový přechod

ApL. na id. plyn (zanedbání  $V_m$  kond. fáze + stavová rovnice):

$$\frac{d \ln p}{dT} = \frac{\Delta H_m^{g \rightarrow l}}{RT^2} \quad \Rightarrow \quad \ln \frac{p_2}{p_1} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \cdot \frac{\Delta H_m^{g \rightarrow l}}{R}$$

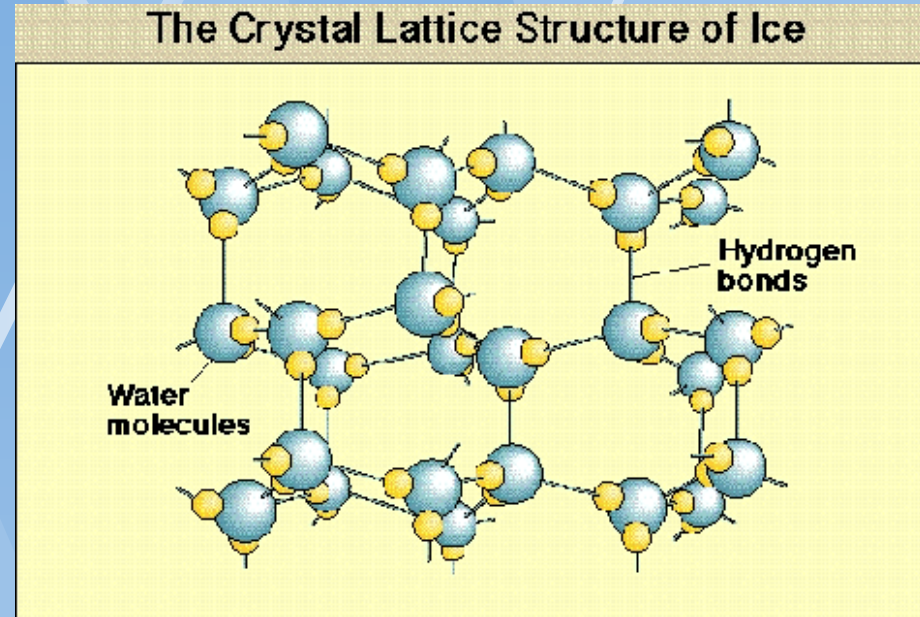
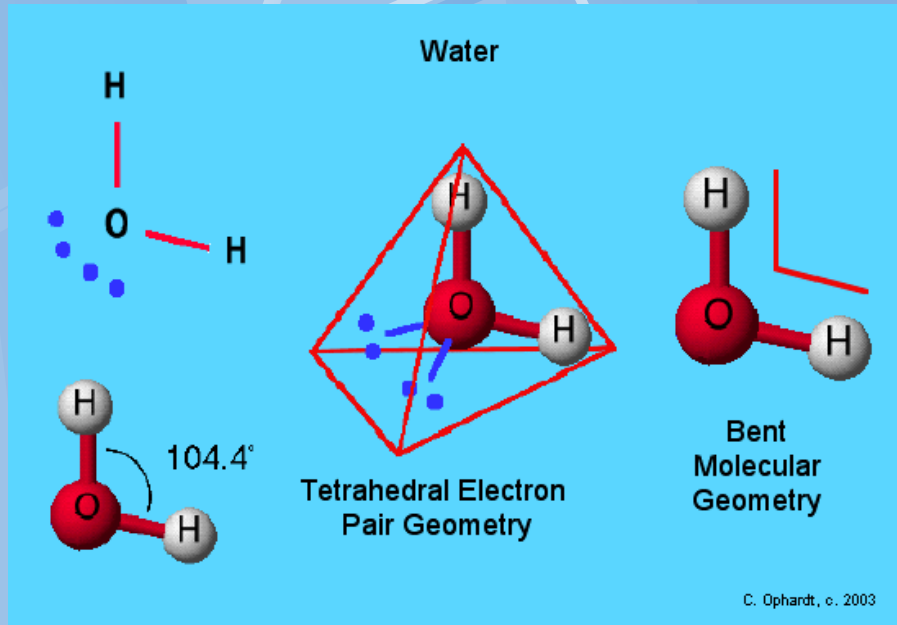
# Vliv p a T na fázové transformace



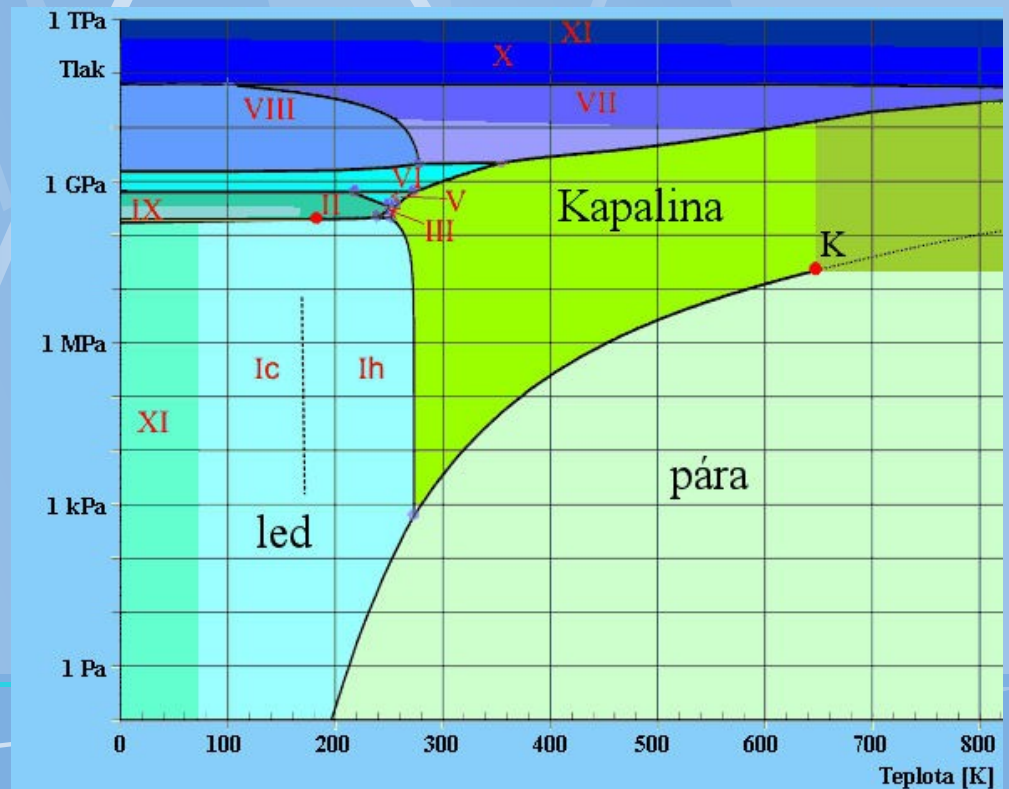
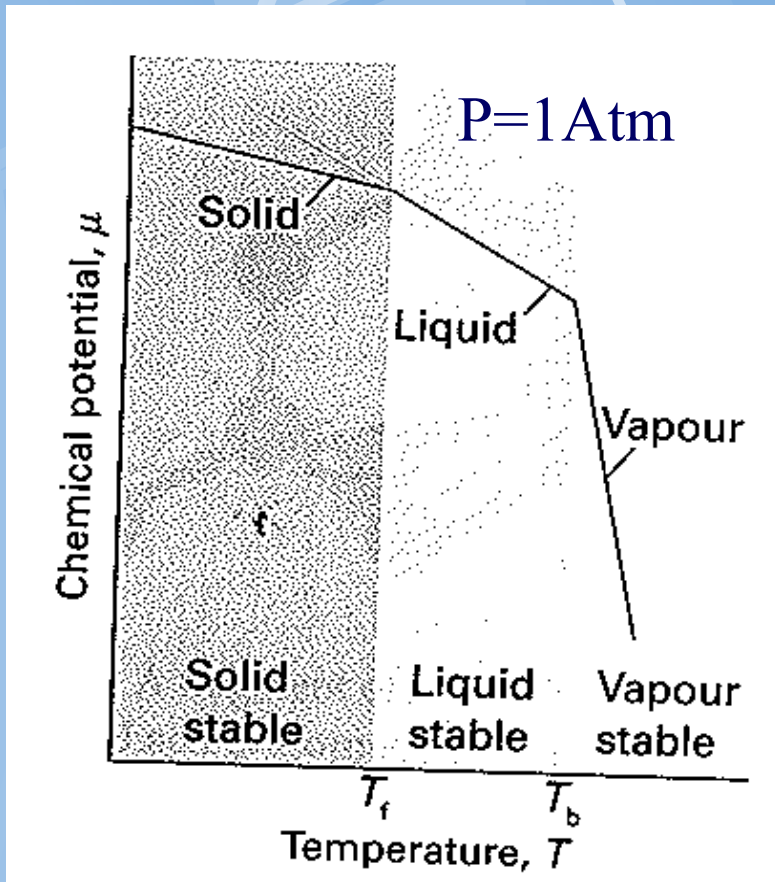
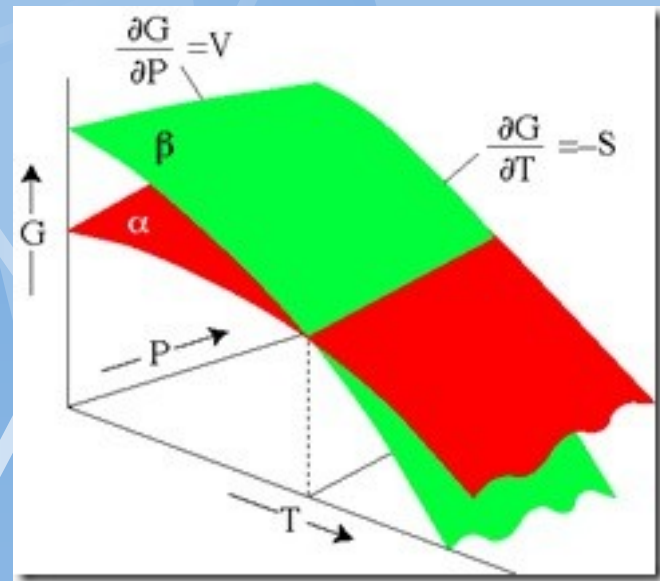
a)  $V_m(s) < V_m(l)$  (většina látek)

b)  $V_m(s) > V_m(l)$  (anomalie vody !!!!)

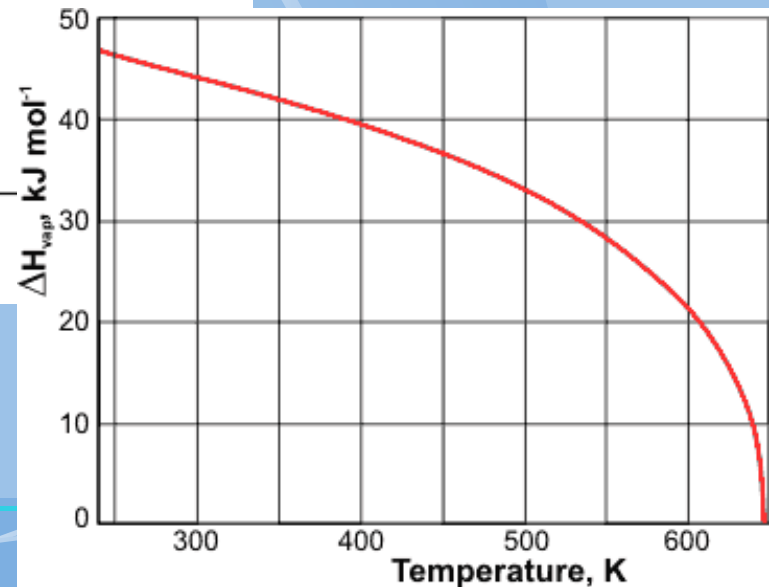
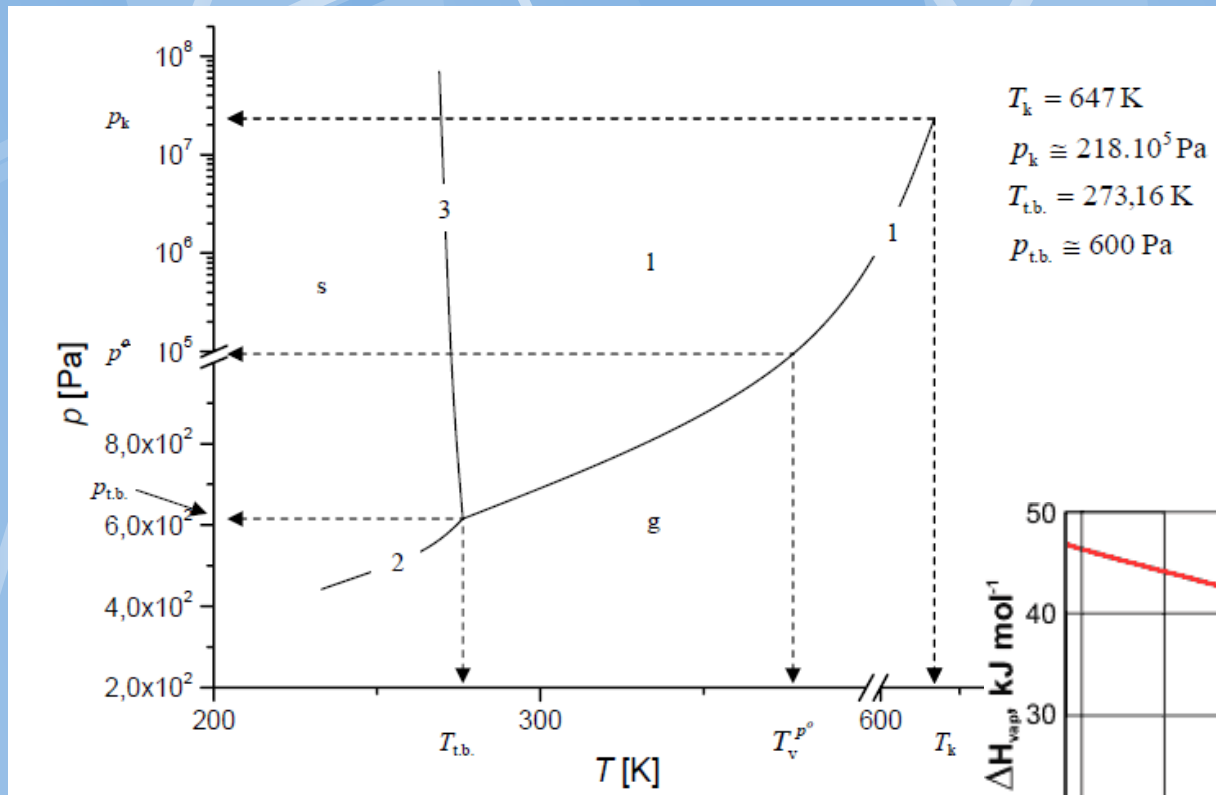
# Obyčejná voda



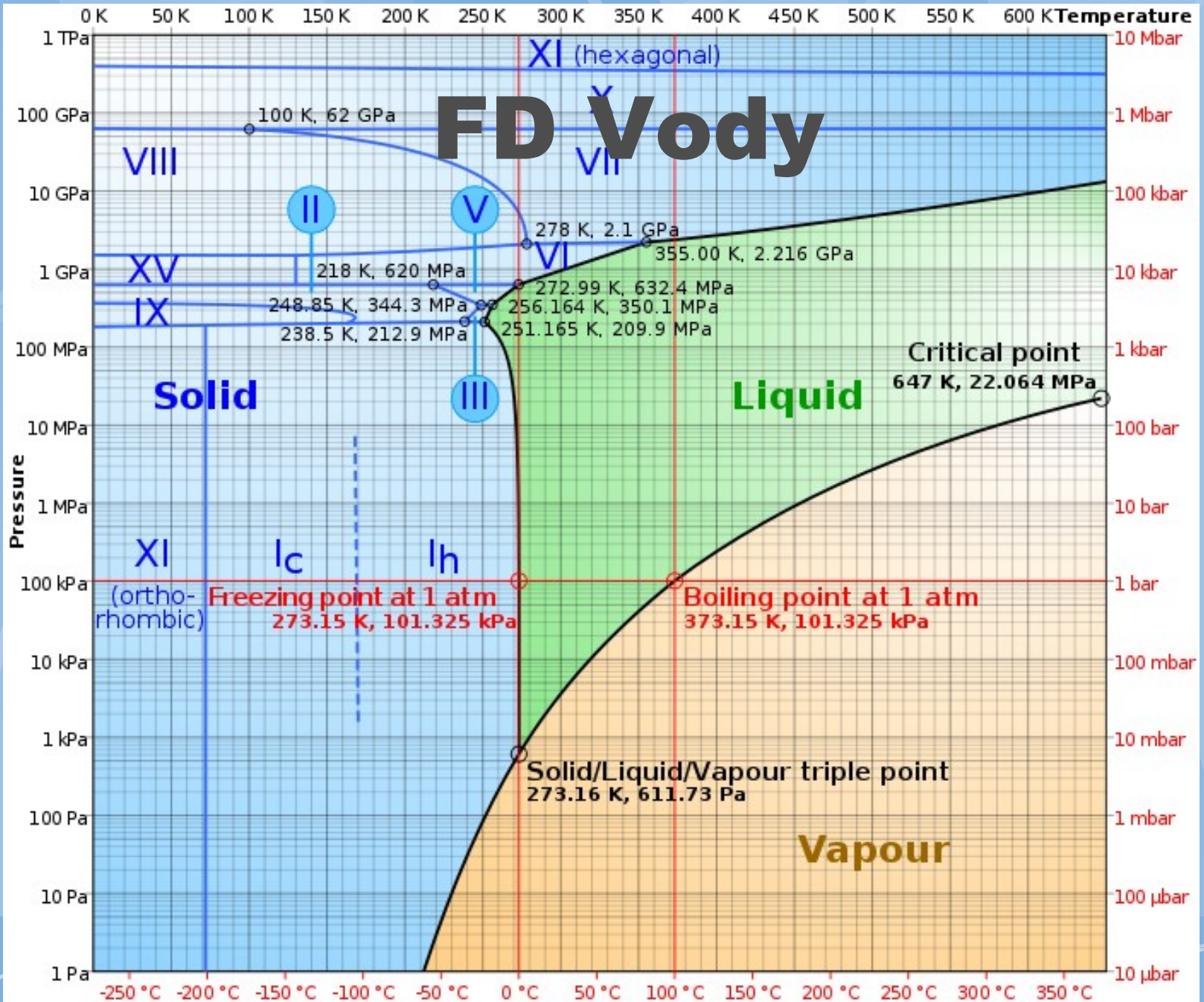
# Gibbsova energije



# Kritický bod g-l vody

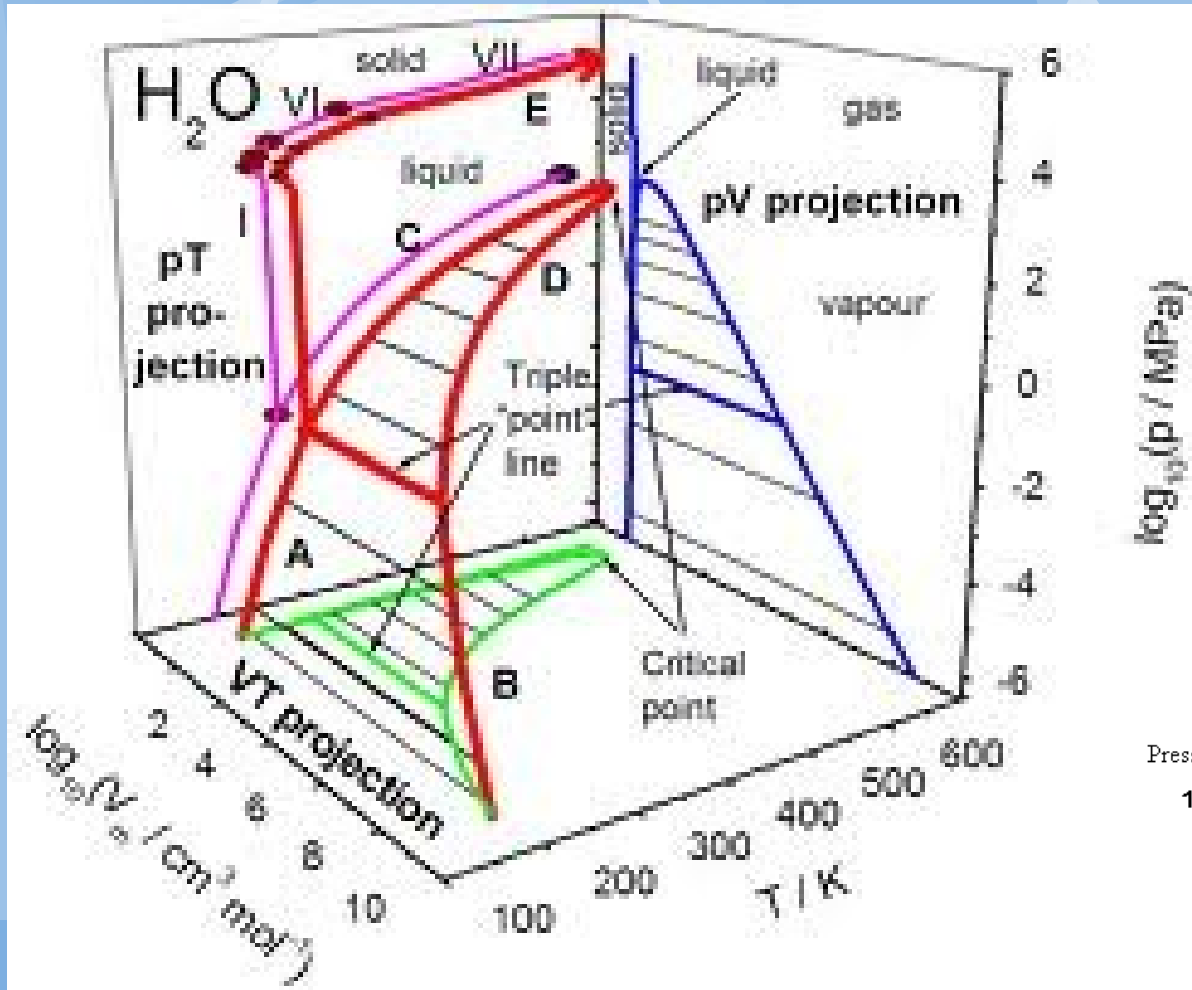




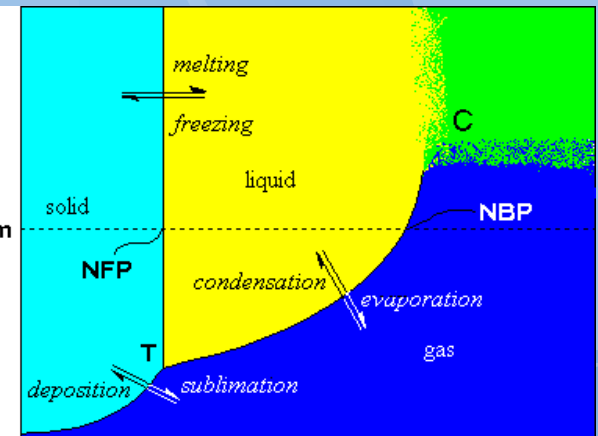




# P-T-Vm projekce



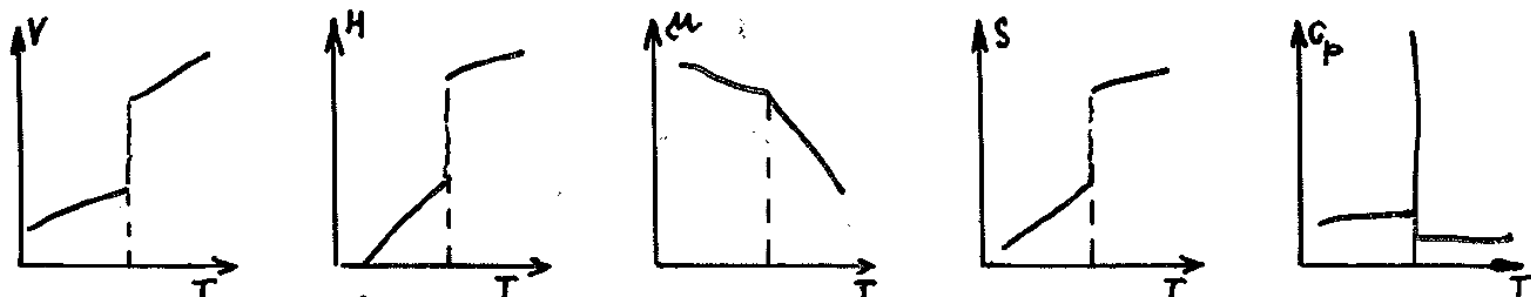
$\log_{10}(p / \text{MPa})$



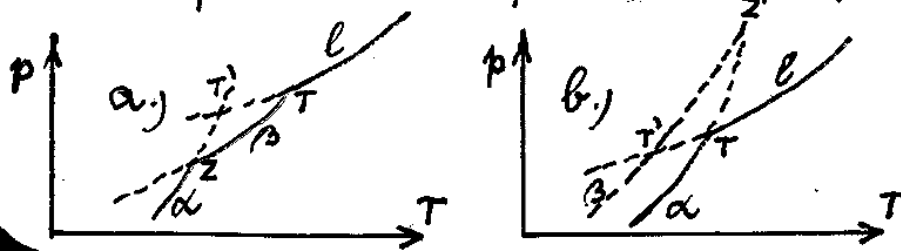
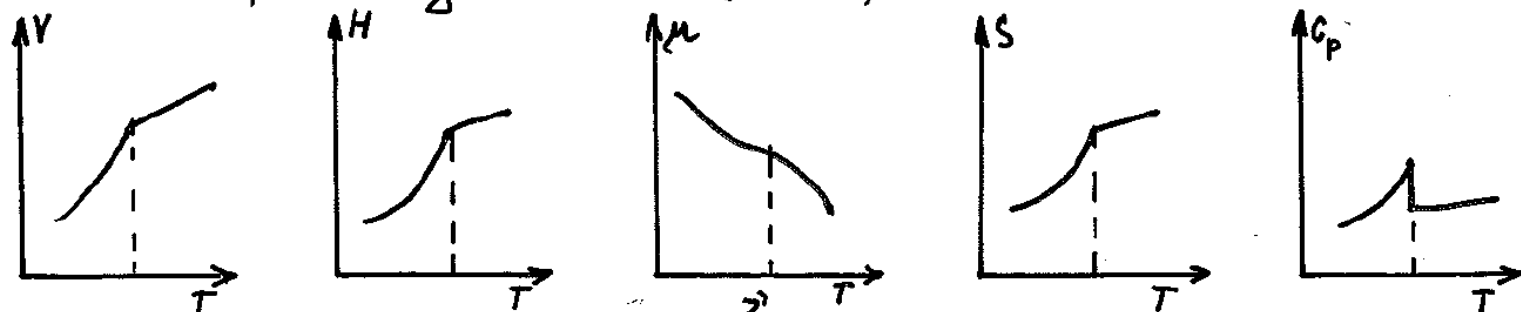
Temperature

# Klasifikace fázových přechodů

## Fázové přechody 1. druhu (řádu)



## Fázové přechody 2. druhu (řádu)



a.) Enantiotropická přeměna  
 b.) monotropická přeměna ( $\beta$  metastabilní)

# Diskuse

Anomálie vody : <http://www.lsbu.ac.uk/water/explan4.html>

The heat of fusion of water with temperature exhibits a maximum at  $-17^{\circ}$  C

Water has over twice the specific heat capacity of ice or steam

The specific heat capacity (CP and CV) is unusually high

The specific heat capacity CP has a minimum at  $36^{\circ}$

The specific heat capacity (CP) has a maximum at about  $-45^{\circ}$  C

The specific heat capacity (CP) has a minimum with respect to pressure

The heat capacity (CV) has a maximum

High heat of vaporization

High heat of sublimation

High entropy of vaporization

The thermal conductivity of water is high and rises to a maximum at about  $130^{\circ}$  C

# Voda



*Out of the bosom of the Air,  
Out of the cloud-folds of her garment shaken,  
Over the woodlands brown and bare,  
Over the harvest-field forsaken,  
Silent, and soft, and slow  
Descends the snow.*

*- Henry Wadsworth Longfellow (1807-1882)*



# Diskuse

