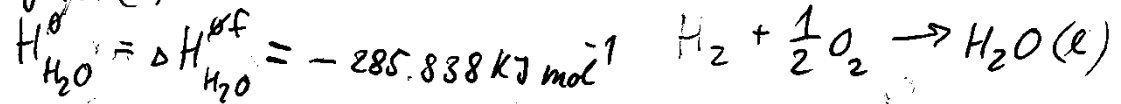


Termodynamika a fázové vlastnosti jednosložkových soustavy



Výpočet ΔG funkcí vody

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



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

$$T_{48}: \Delta S_{H_2O}^\circ = -163,292 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{H_2}^\circ = 130,587 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{O_2}^\circ = 205,29 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

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

$$H(T) = H^\circ + \int_{T^\circ}^T C_p^m dT = H^\circ + C_p^m \cdot (T - T^\circ) = -280184 \text{ J mol}^{-1}$$

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

$$G(T) = H(T) - T \cdot S(T) = -312594 \text{ J mol}^{-1}$$

Výpočet pro tlak $p = 50 \text{ atm}$

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

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

$$= -312594 + 18 \cdot 10^{-6} \cdot (50 - 1) \cdot 101325 = -312505 \text{ J mol}^{-1}$$

Fázový přechod

$$T_{AB}: 1 \text{ atm}:$$

| $T [K]$ | $\Delta H_{vap} [kJ mol^{-1}]$ |
|---------|--------------------------------|
| 298 | 44.01 |
| 373 | 40.67 |

$$H_{H_2O}^g(373K) = H_{H_2O}^l(373) + \Delta H_{vap}(373, 1 \text{ atm}) = -280184 + 40.67 \cdot 10^3 =$$

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

ΔH_{vap}

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

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

Plynový stav: $T=473K$, $p=1 \text{ atm}$, H_{Gas} . $P_{H_2O}(373-500K)$

$$H(T) = H^g(373) + \int_{T_v}^T C_p dT =$$

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

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

TAB: $C_p^m(g) = 30.12 + 11.30 \cdot T$
[J mol⁻¹ K⁻¹]

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

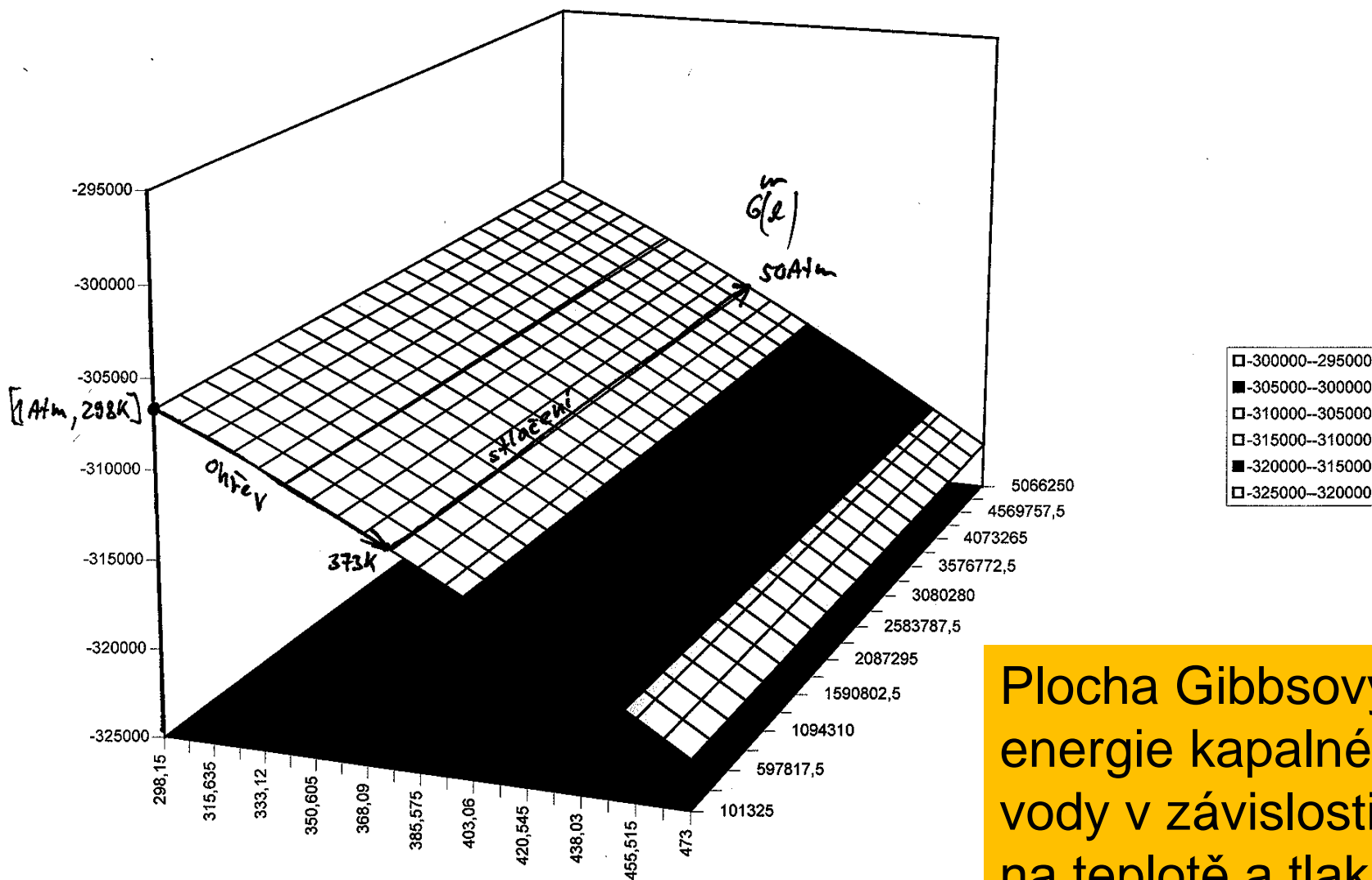
$$= S^g(373) + a \cdot \ln \frac{T}{T_v} + b \cdot (T - T_v) = \underline{\underline{1332.997 \text{ J mol}^{-1} K^{-1}}}$$

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

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

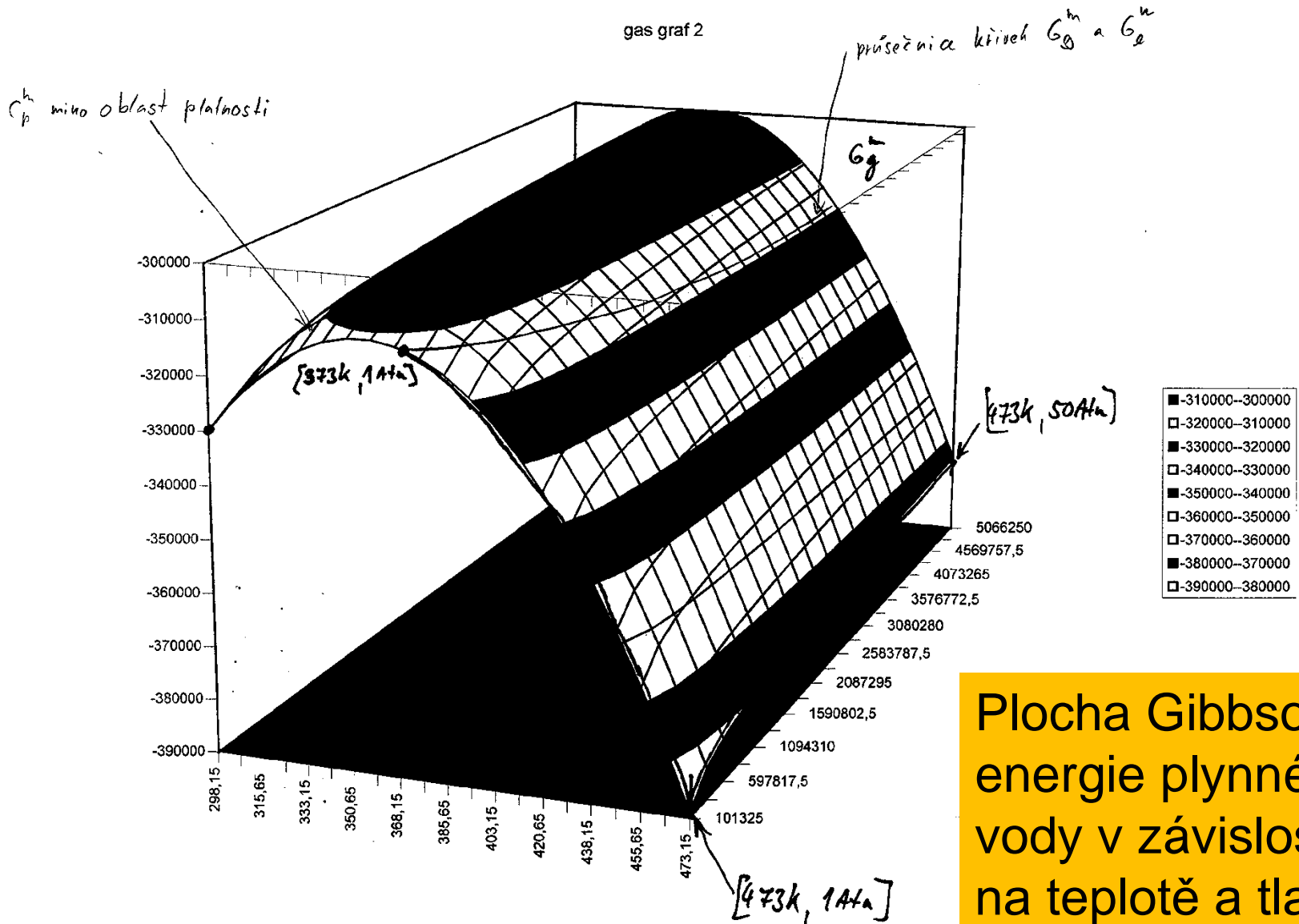
$$G(p) = G(p_g) + RT \ln \frac{p_g}{p} = -389050 + 8.314 \cdot 473 \cdot \ln \frac{50}{1} =$$

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



Plocha Gibbsovy energie kapaln  vody v z vislosti na teplot  a tlaku

gas graf 2



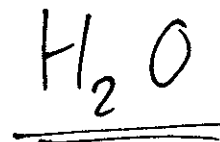
Plocha Gibbsovy energie plyné vody v závislosti na teplotě a tlaku

1 Atm
↓

List5

50 Atm
↓

výpočet
hranice fázových
oblastí l-g
pro soustavu

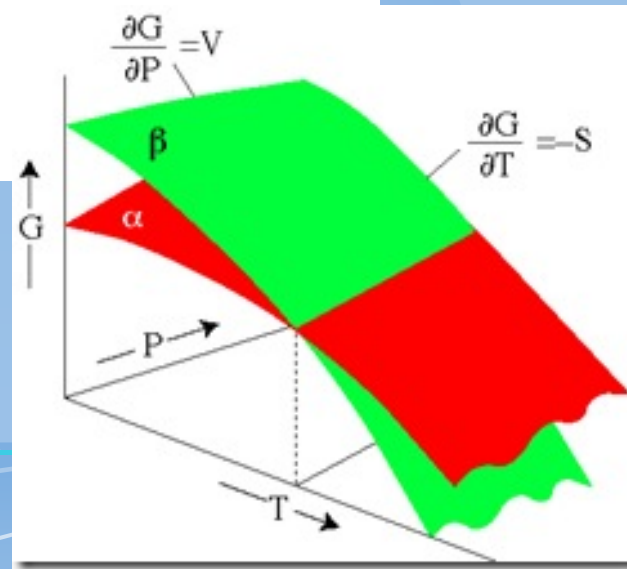
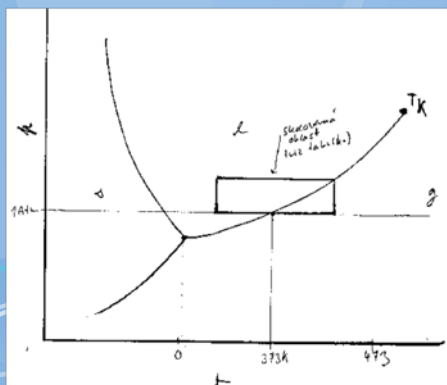


minimální
index
podstati
C_p

(l→g)
hranice veče
přibližně zde

373K=100°C

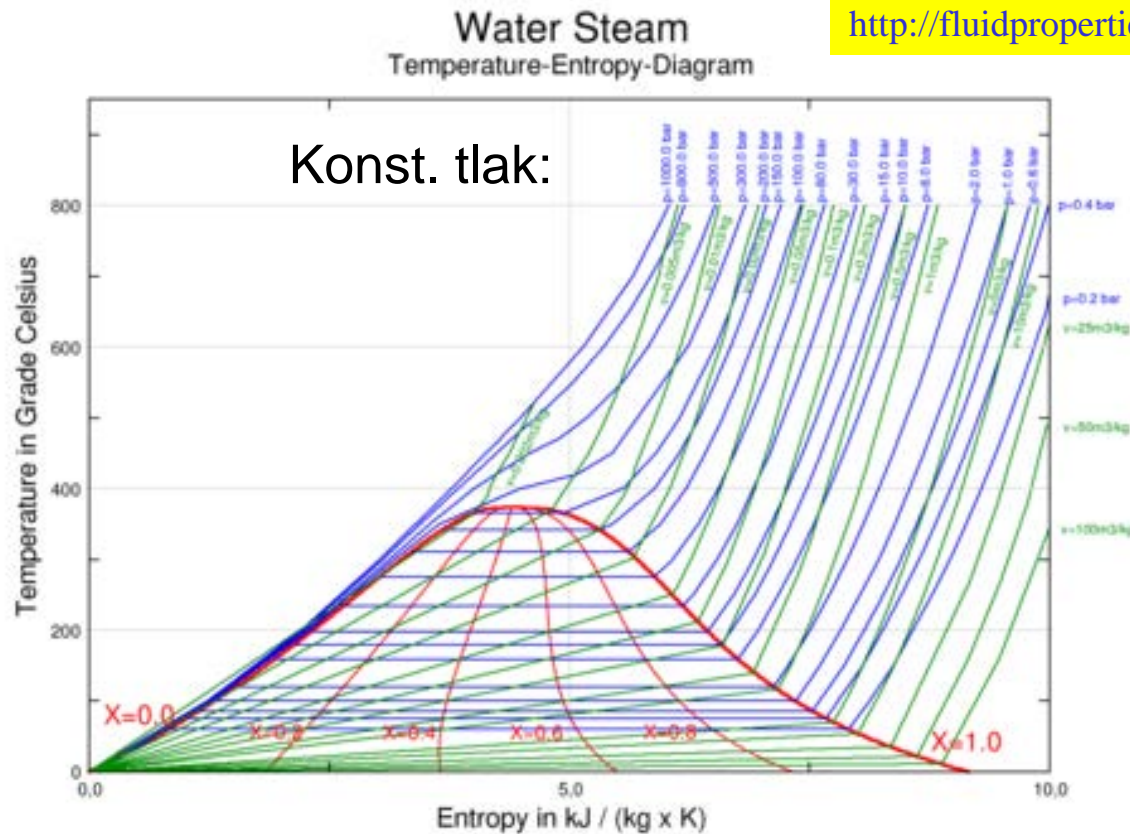
| G(liquid)-G(gas) T [K] P [Pa] | 101325 | 1094310 | 2087295 | 3080280 | 4073265 | 5066250 |
|----------------------------------|----------|----------|----------|----------|----------|----------|
| 298,15 | 23240,29 | 17359,36 | 15776,46 | 14829,64 | 14154,83 | 13631,91 |
| 306,8925 | 17294,57 | 11240,52 | 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 |



Fázové diagramy a termodynamické funkce různých kapalin:

<http://fluidproperties.blogspot.cz/>

Konst. tlak:



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 **isochors** showing constant specific volume. The red curves show constant quality.

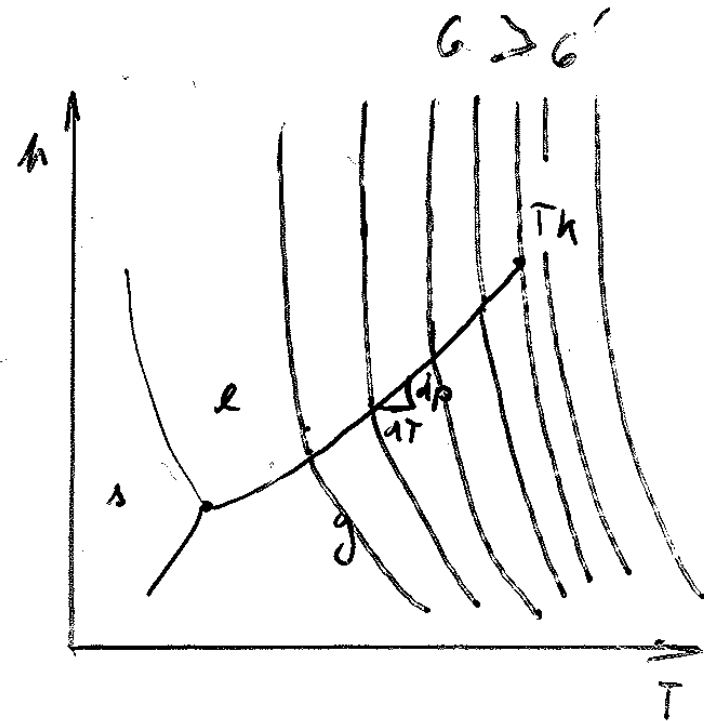
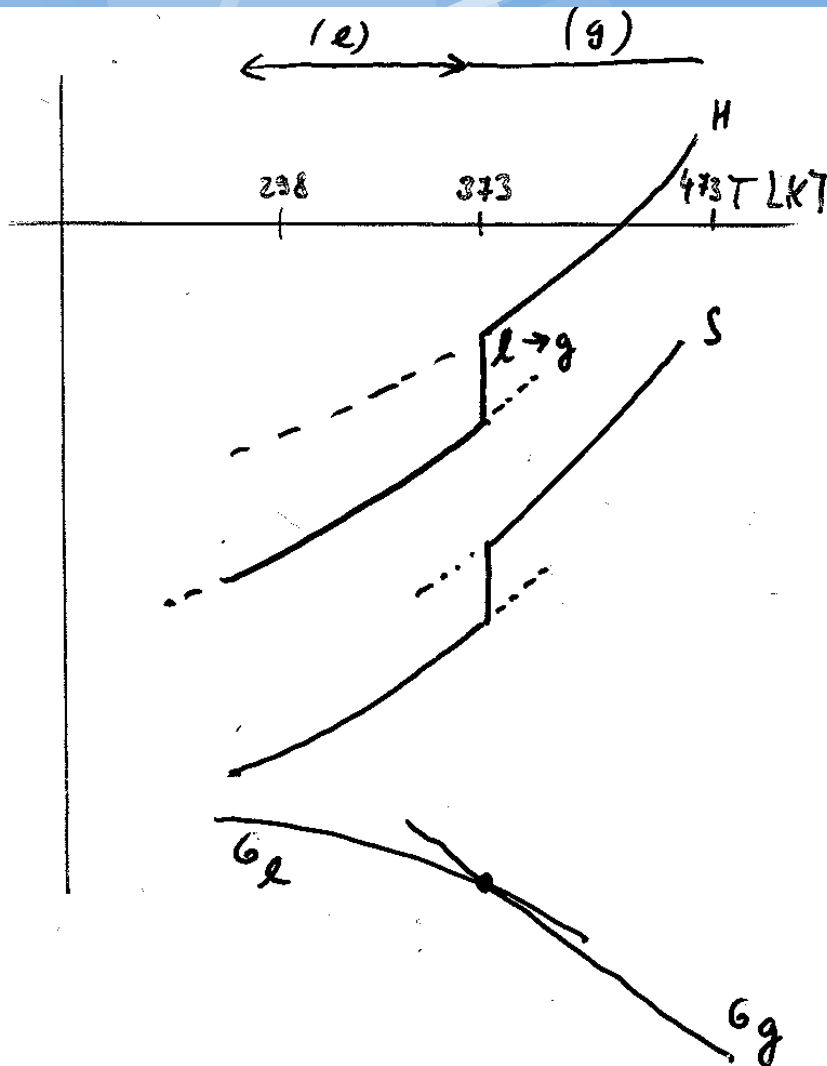
Read more: <http://www.answers.com/topic/phase-diagram#ixzz2fheybptD>

Závěry k příkladu H₂O (platí obecně)

- ① z experimentálních 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 ($C_p, \Delta H_{f1 \rightarrow f2}, S^s, \dots$)
- ⑥ Je třeba sledovat interval platnosti exp. fázových dat $\Delta H_{f1 \rightarrow f2}, C_p$ (pozor na $\Delta H_{0,p}$).

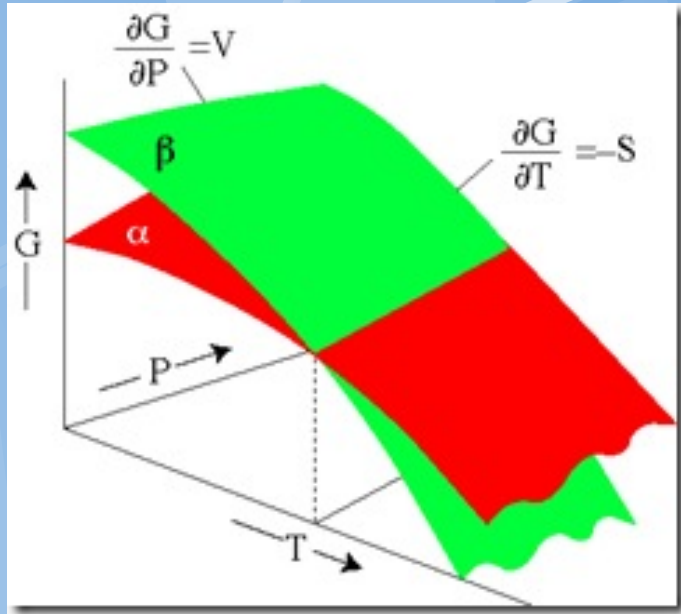
7. Molární Gibsova energie je pro čistou látku rovna jejímu Chemickému potenciálu.

Text konzistence TD dat



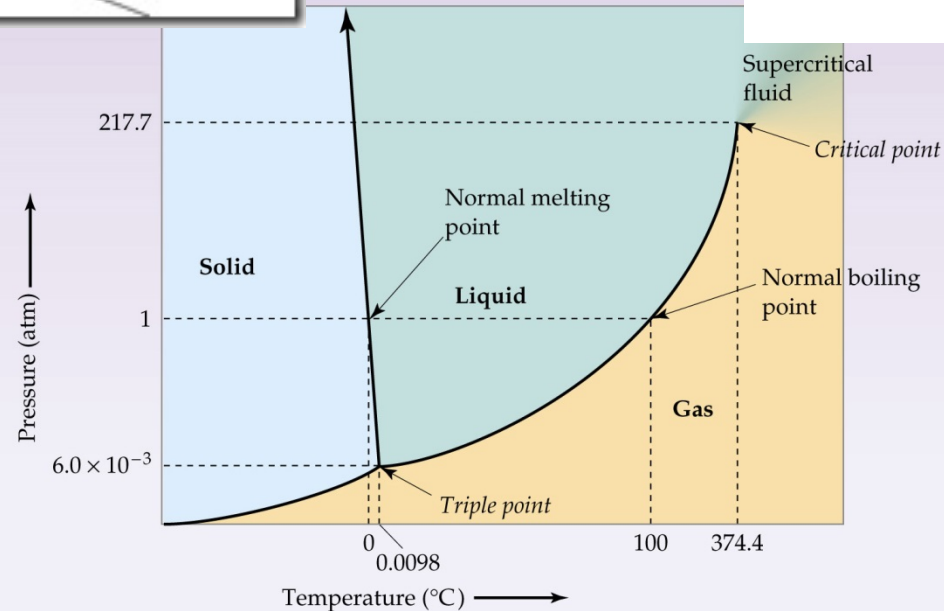
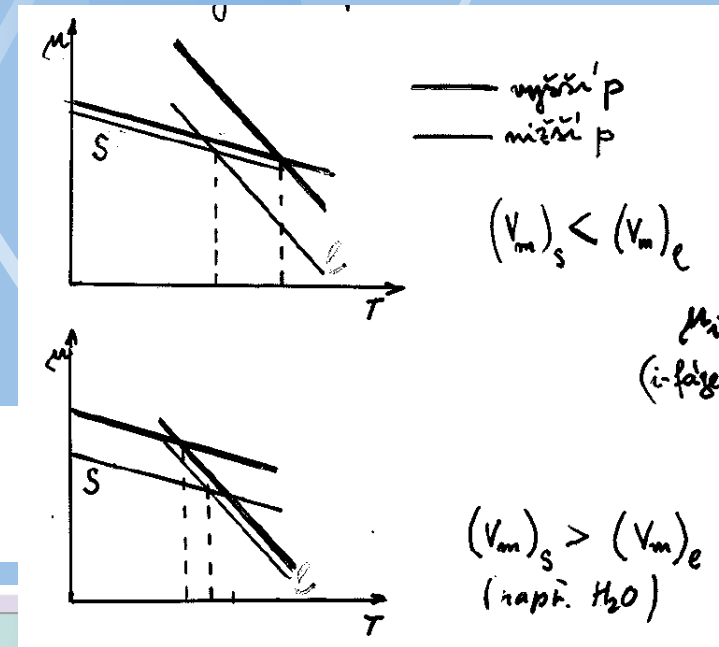
- ⊗ pozor pokud kombinujeme f -a pro různé fáze
- ! Test konzistence

Jednosložkové fázové diagramy



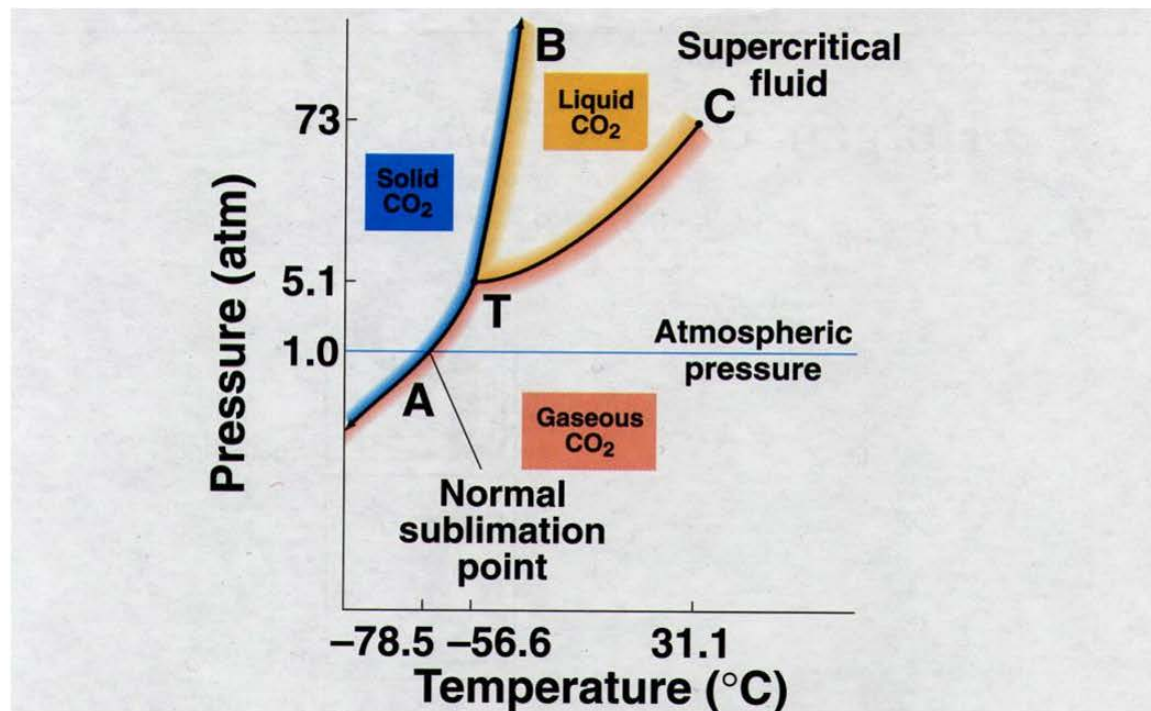
● H₂O

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

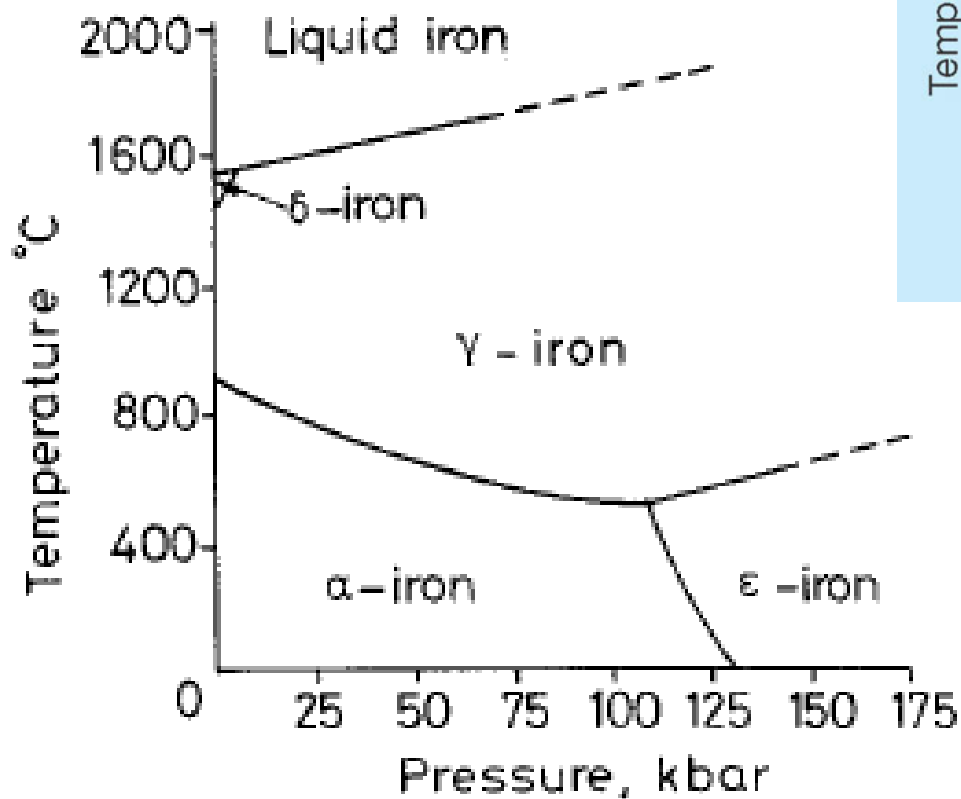
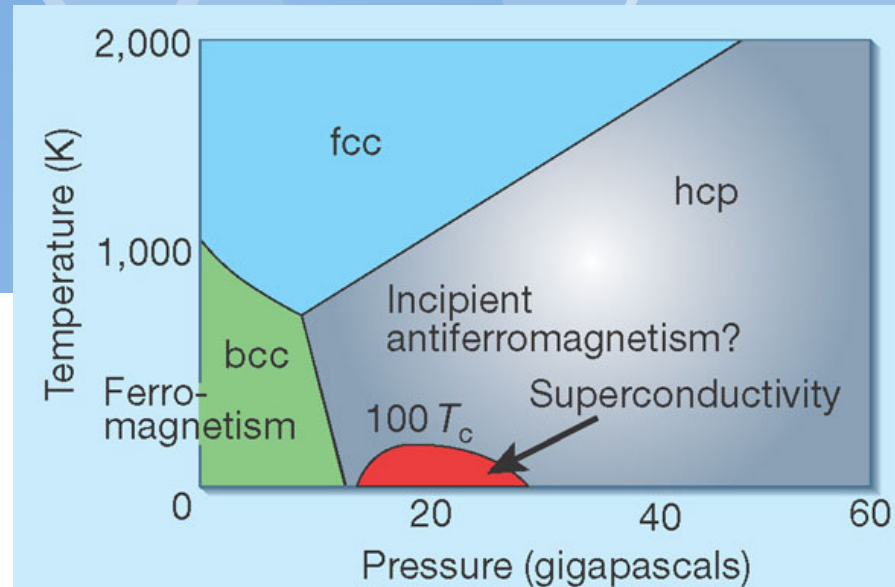


CO₂

Phase Diagram for CO₂

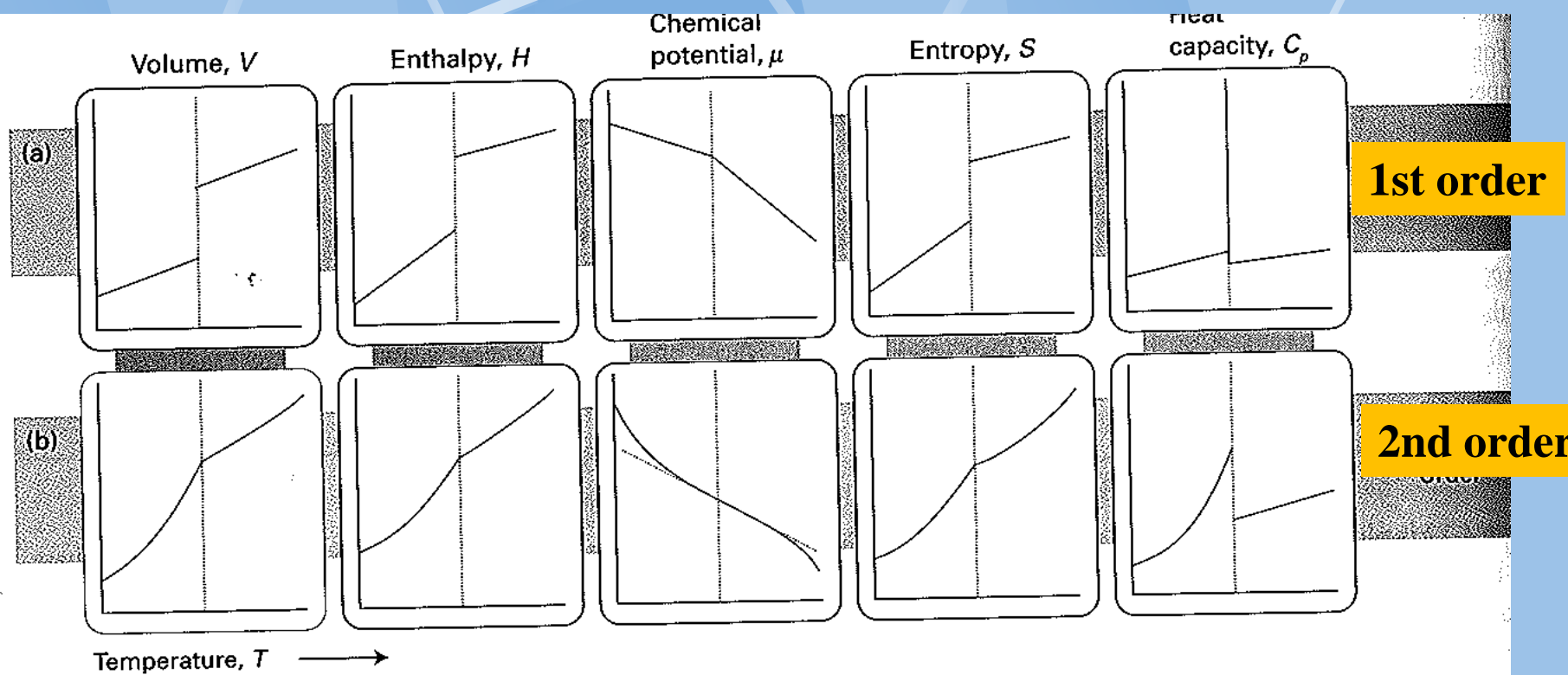


FD železa



Predikce fází

Klasifikace fázových přechodů



TD Kritérium 1.
řádu:

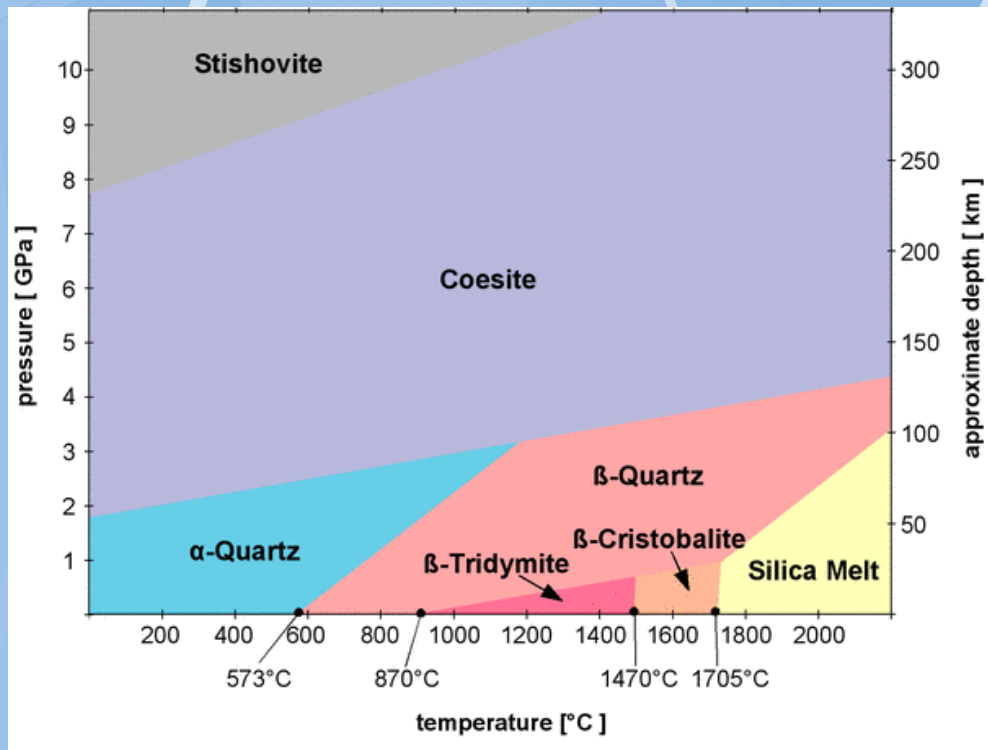
Jeli FT provázána
skokovou změnou
objemu a entropie
jde o FT 1. řádu

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

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

Příklady řechodů 1. druhu

Přemístění složek, atomů, iontů, atd.



Gallium

$T_m = 29,7645^{\circ}\text{C}$,
(302,9145 K)

SiO_2

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:

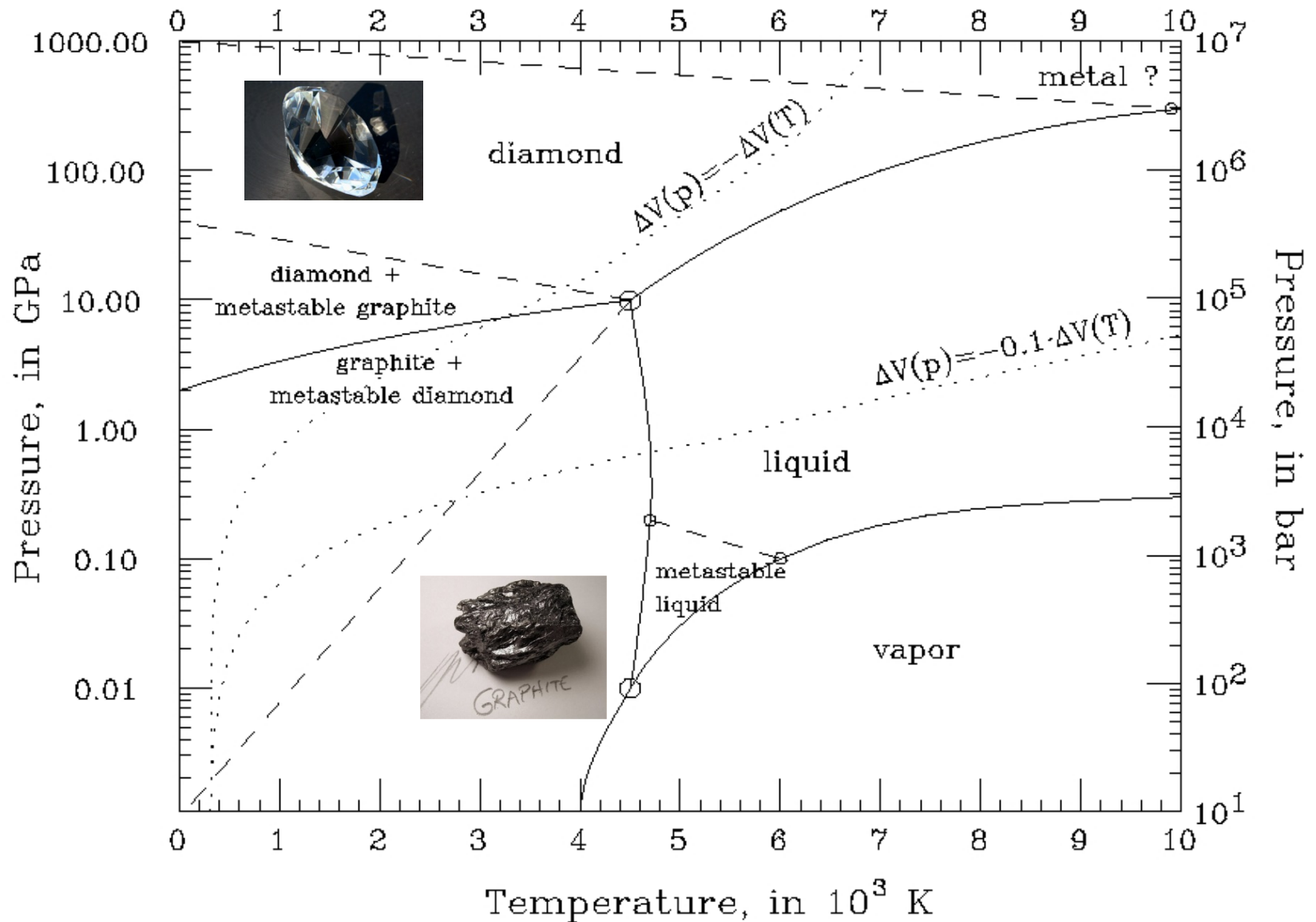
$$\Delta S_{m \rightarrow l}^{\circ} = \frac{\Delta H_{m \rightarrow l}^{\circ}}{T}$$

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

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

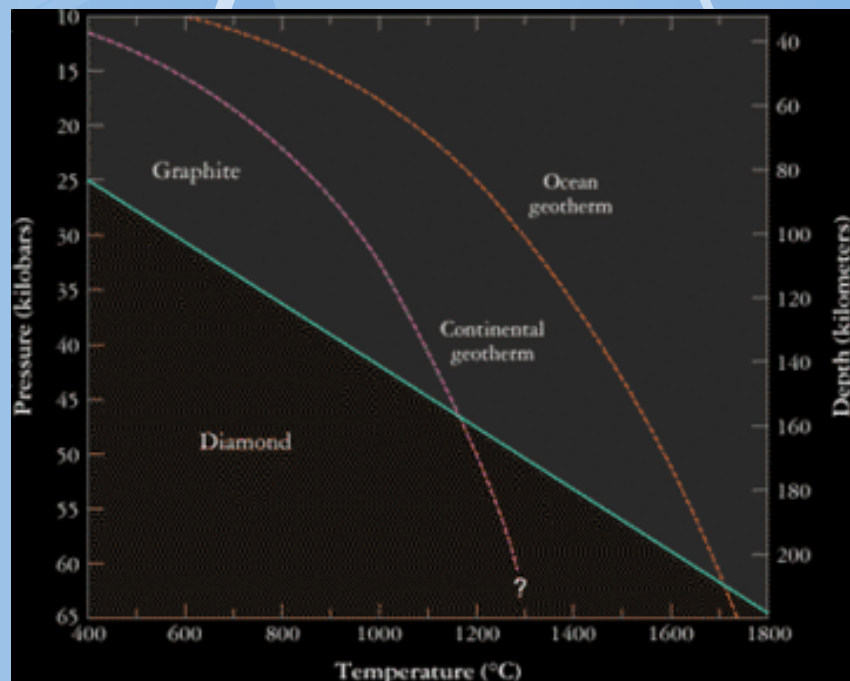
37-59 J/molnízkomolekulární organické látky

FD Uhlíku



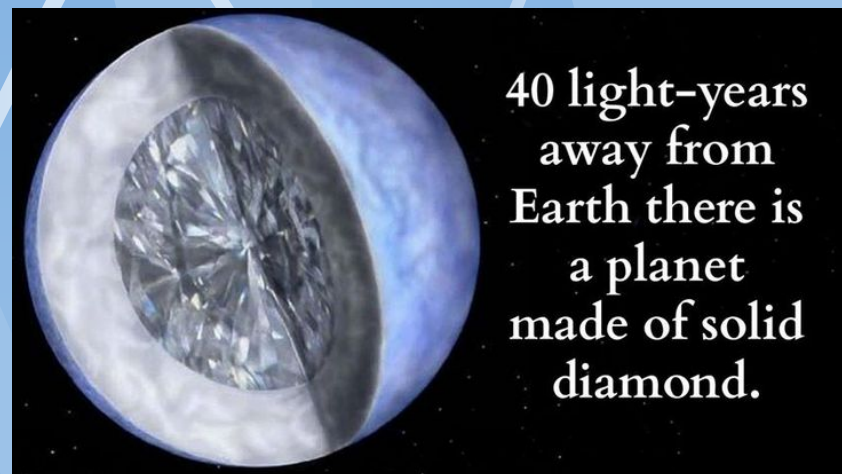
Vznik diamantů

Na Zemi



<http://www.amnh.org/exhibitions/permanent-exhibitions/earth-and-planetary-sciences-halls/morgan-memorial-hall-of-gems/hall-of-gems-promos/for-educators/where-do-diamonds-come-from>

Na jiných planetách



40 light-years
away from
Earth there is
a planet
made of solid
diamond.

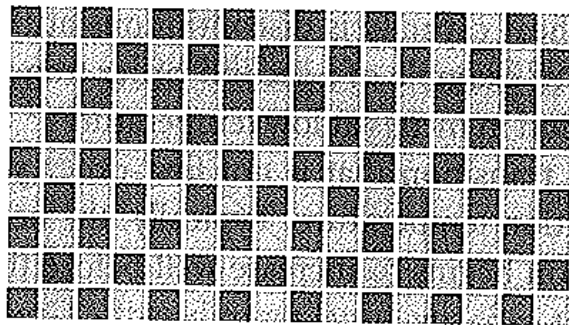
http://www.dailygalaxy.com/my_weblog/2007/11/a-diamond-bigge.html

Příklady přeměn 2 druhu

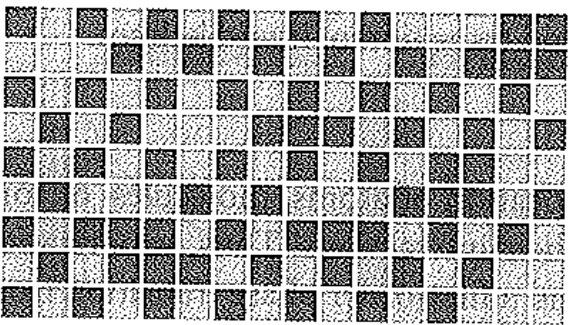
Změny symetrie

Uspořádací přeměny

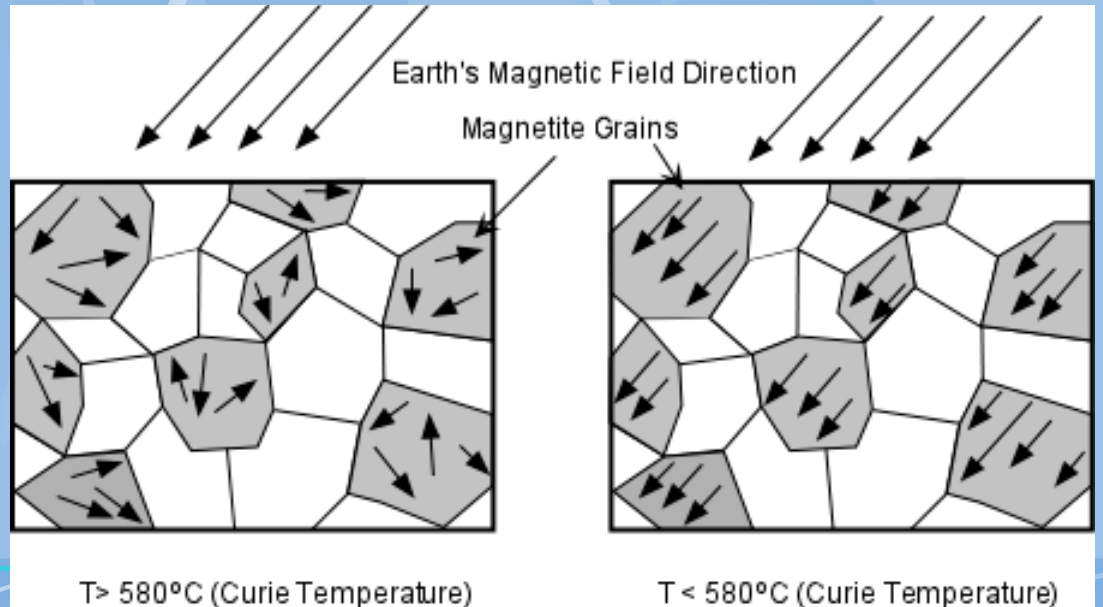
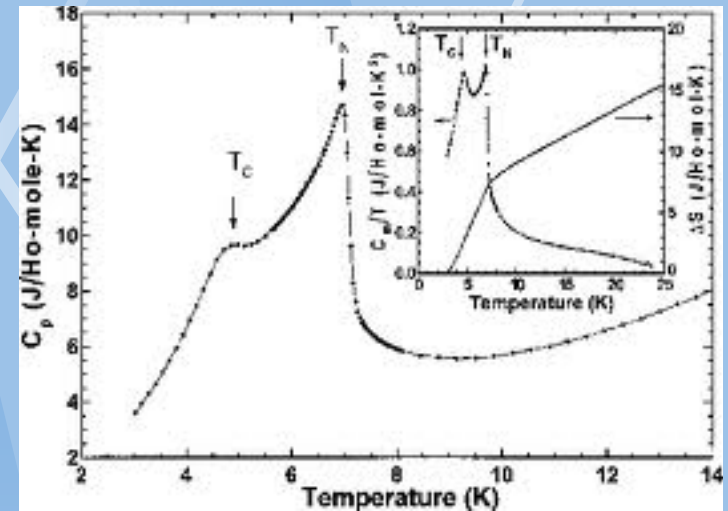
Ordering,
magnetization,



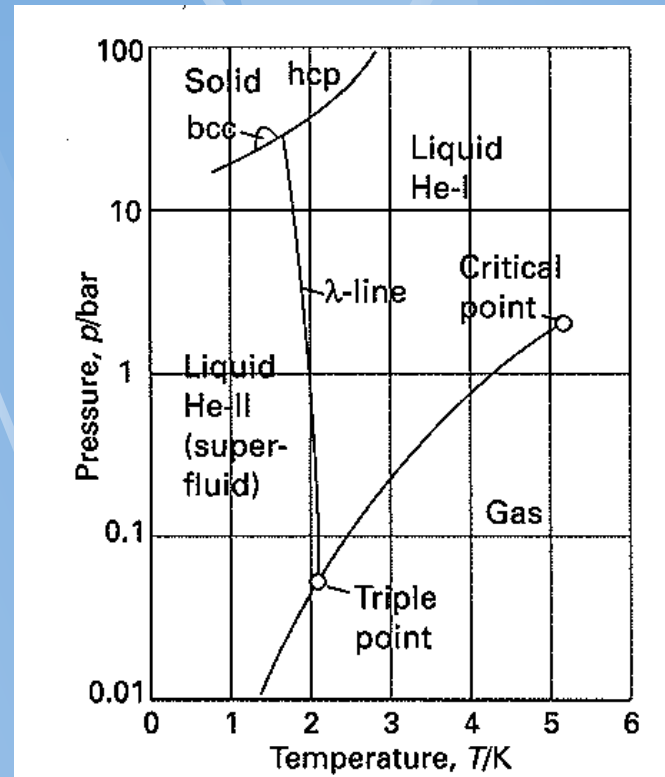
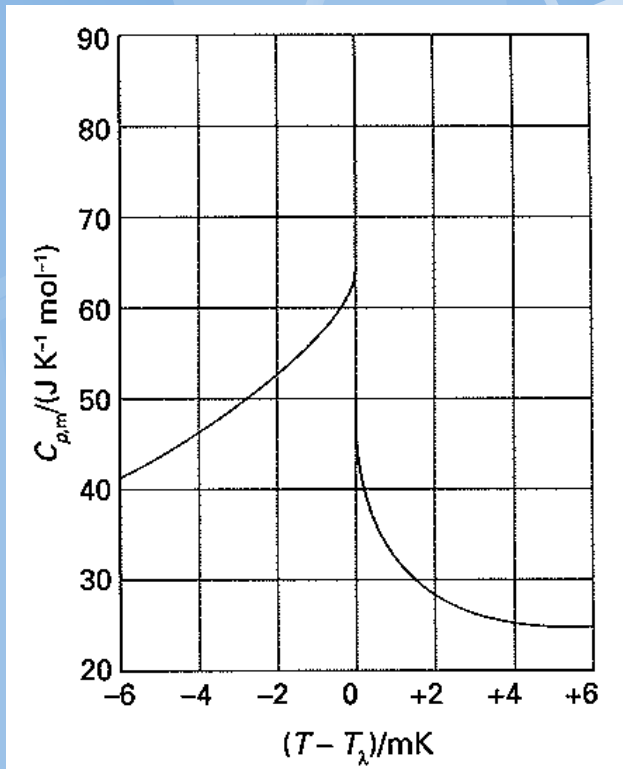
(a)



(b)



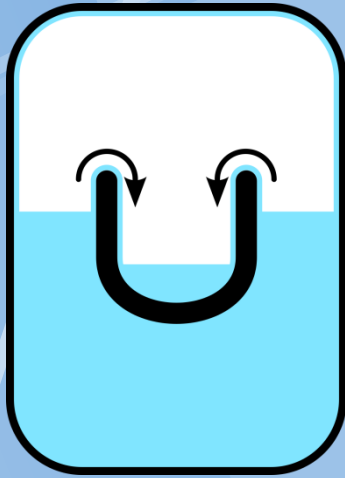
Supravodivost He



The λ -curve for helium,

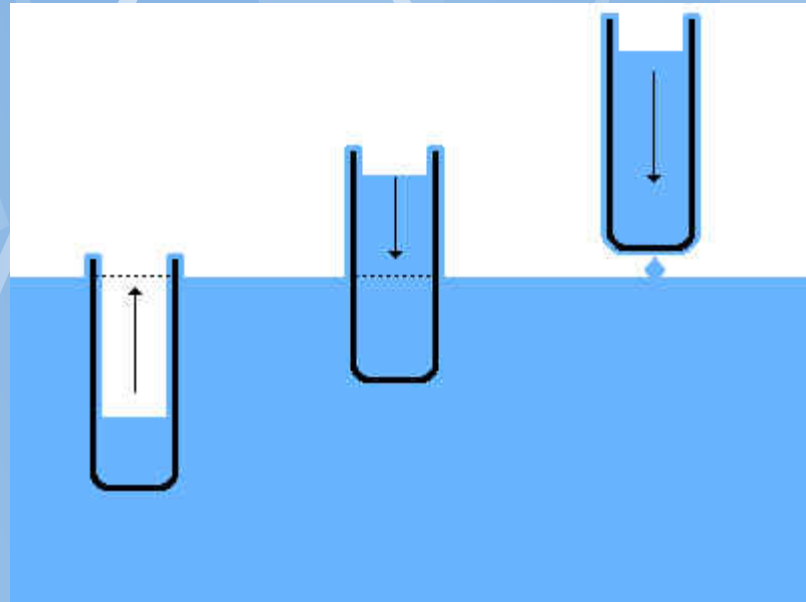
Supravodivá oblast helia

Superliquid He



Superfluid
(zero
viscosity)

<https://en.wikipedia.org/wiki/Superfluidity>



Clausius-Clapeyronova rovnice

Obečné odvození Clausius-Clapeyronovy r-ice

Taylorův rozvoj

Na ploše $G^g(T, p)$:

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

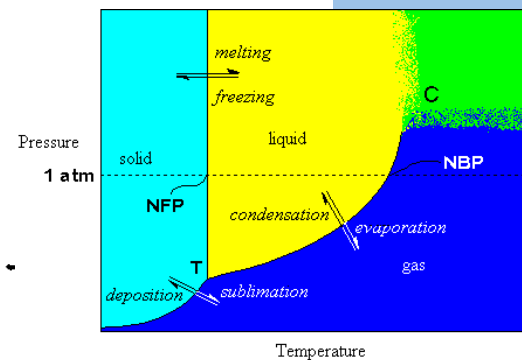
Na ploše $G^l(T, p)$:

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

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

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

Další (12)-(14) dle...



Pak (13)-(14) dá:

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

po úpravách

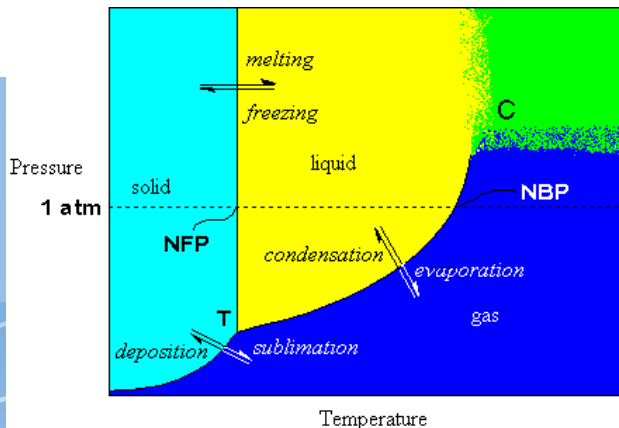
$$\boxed{\frac{dp}{dT} = \frac{\left(\frac{\partial G^g}{\partial T}\right)_p - \left(\frac{\partial G^l}{\partial T}\right)_p}{\left(\frac{\partial G^g}{\partial p}\right)_T - \left(\frac{\partial G^l}{\partial p}\right)_T} = \frac{s^g - s^l}{v^g - v^l} = \frac{\Delta S_m^{g \rightarrow l}}{\Delta V_m^{g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

obecná C.C. rovnice

• platí obecně pro jakýkoliv fázový přechod

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

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2} \Rightarrow \ln \frac{p_2}{p_1} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \cdot \frac{\Delta H_{vap}}{R}$$



Vliv p a T na fázové transformace

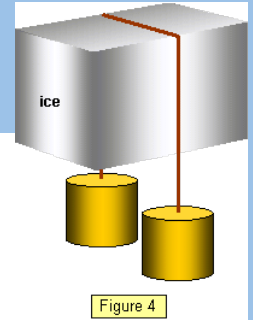
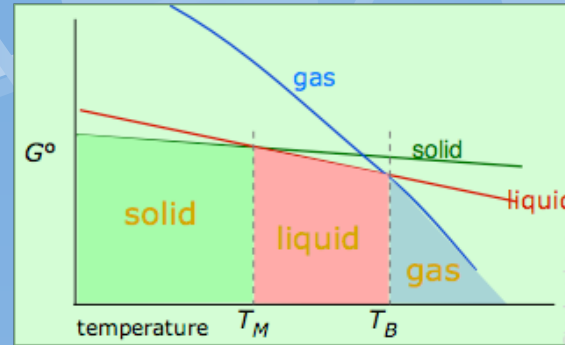
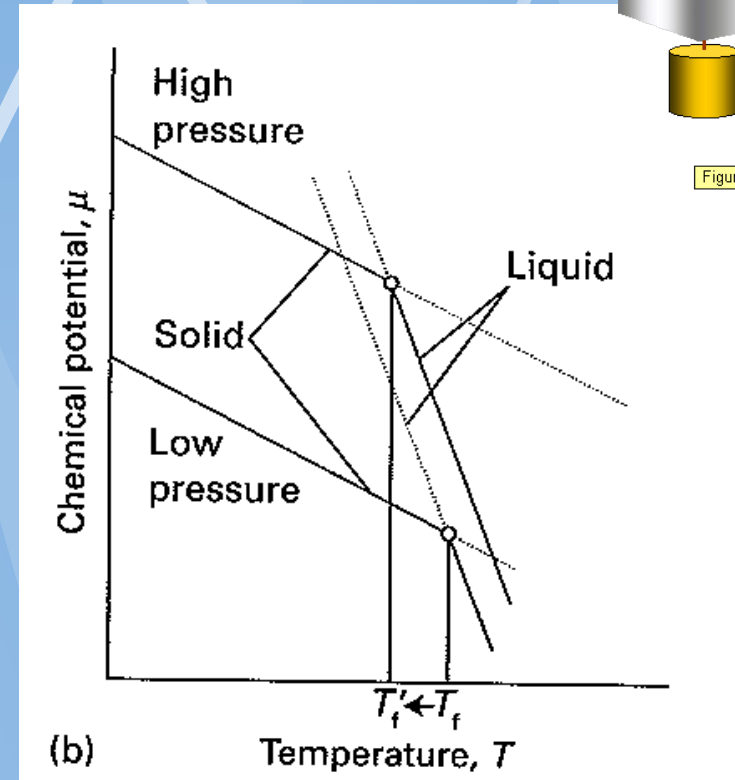
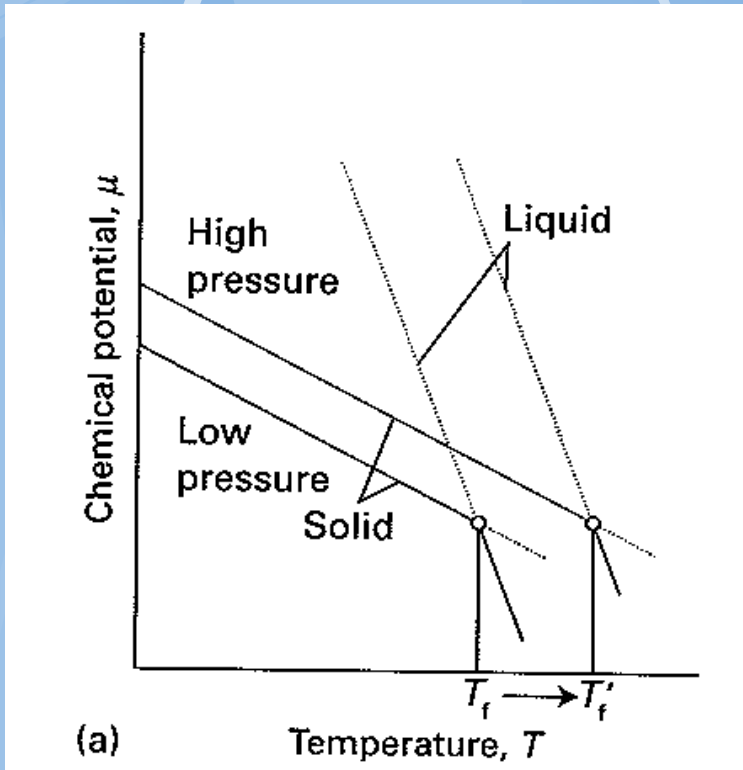


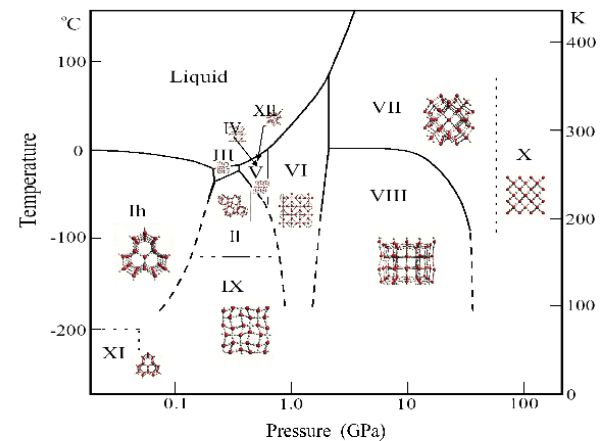
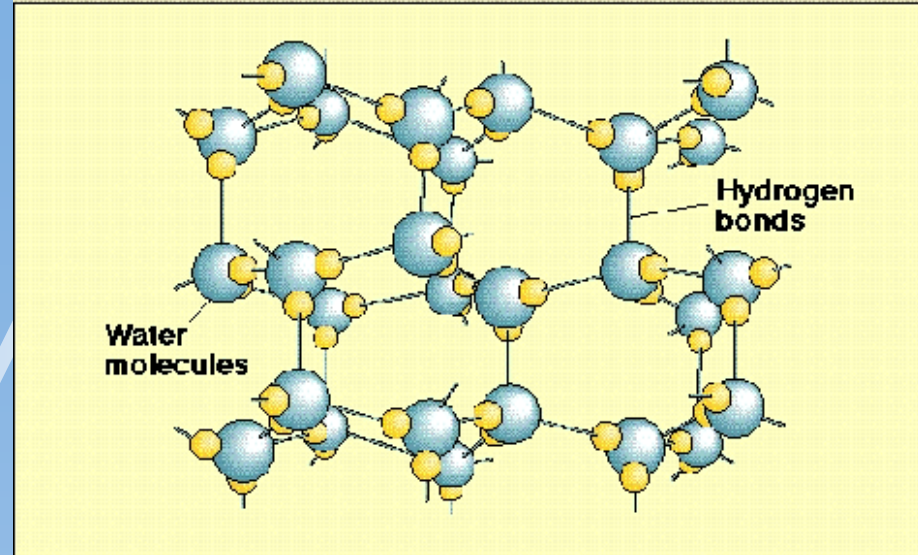
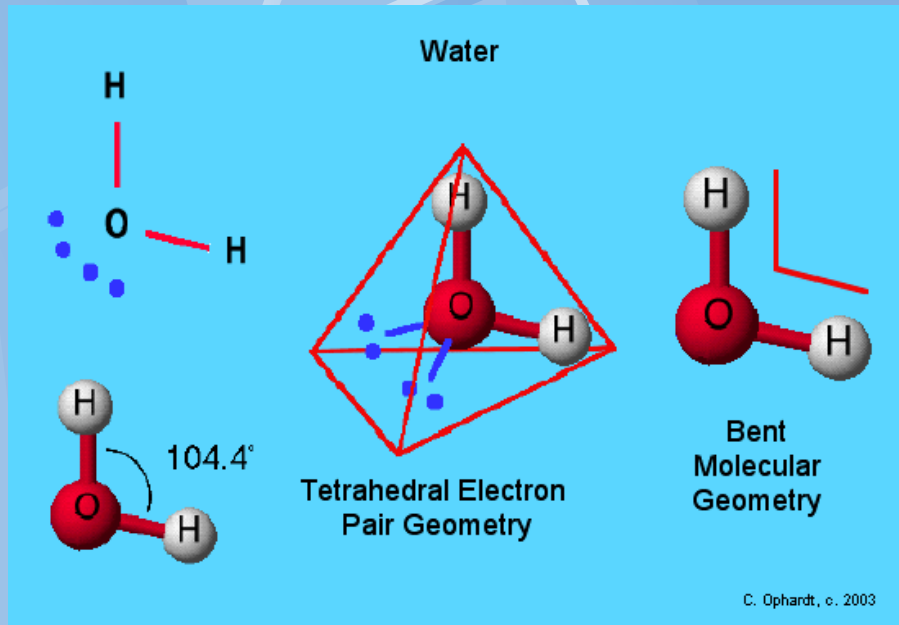
Figure 4



a) $V_m(s) < V_m(l)$ (většina látek) b) $V_m(s) > V_m(l)$ (anomalie vody !!!!)

Obyčejná voda

The Crystal Lattice Structure of Ice



Anomálie vody

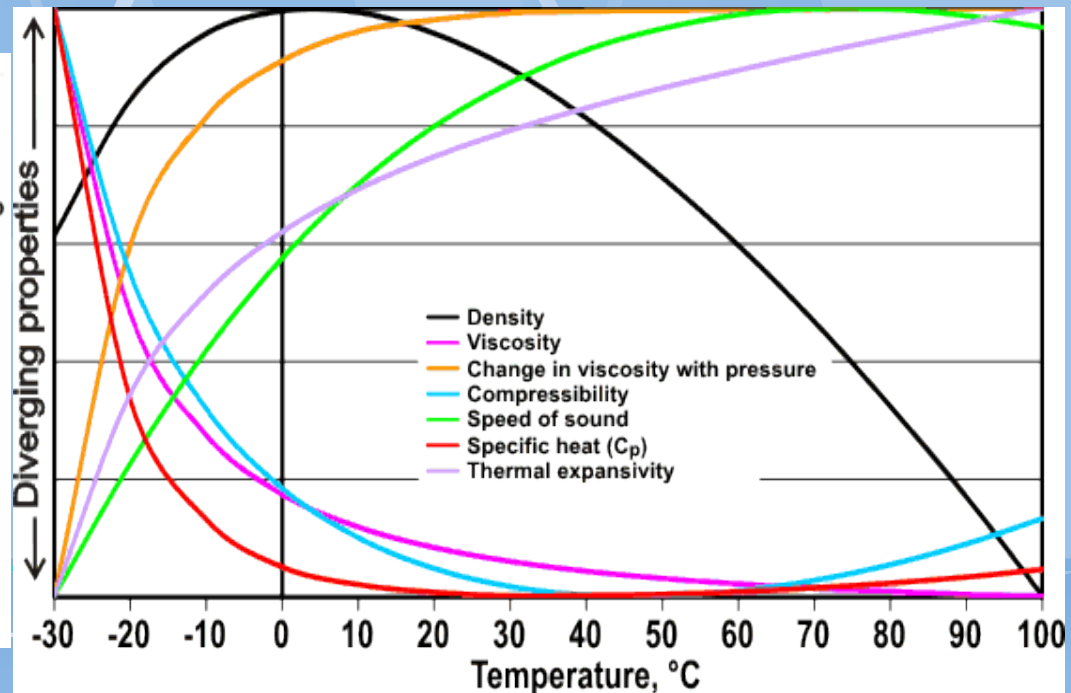
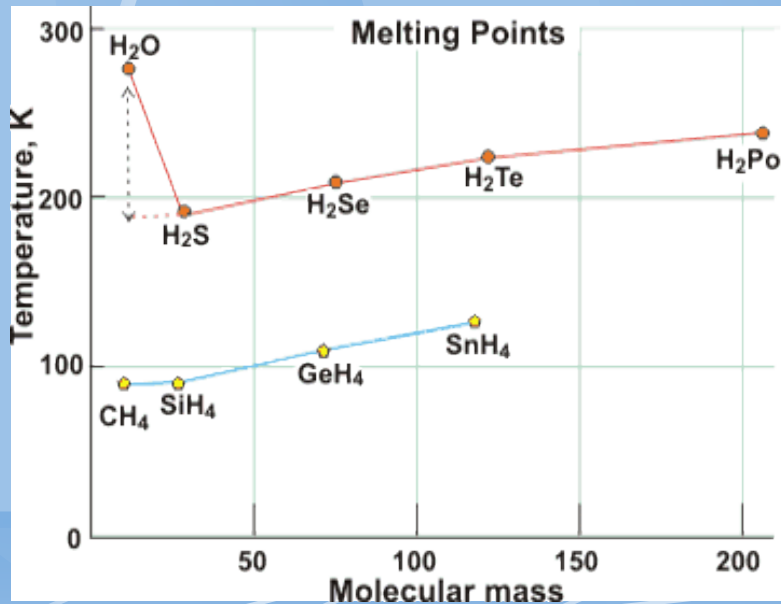
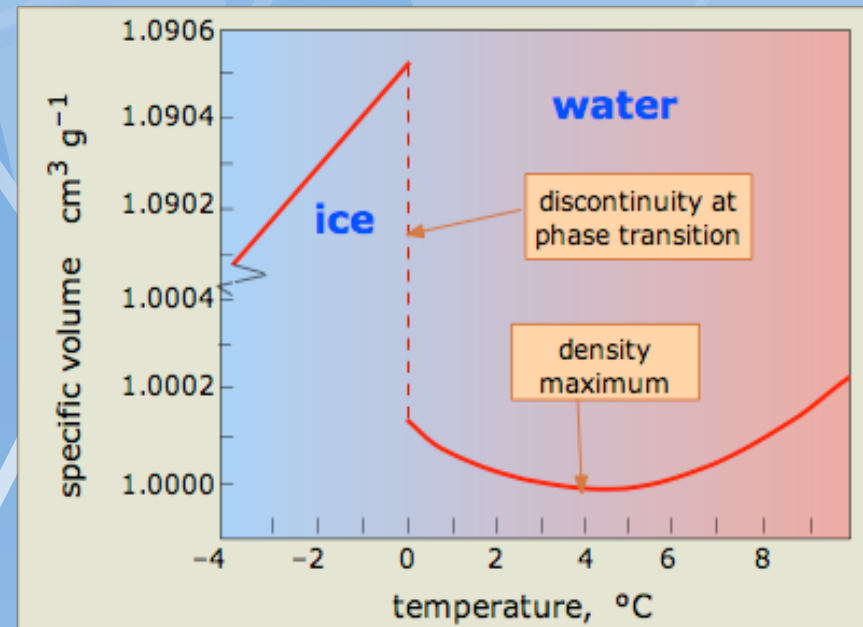
(popsáno 41 anomálií :-)

<http://www.chem1.com/acad/sci/aboutwater.html>

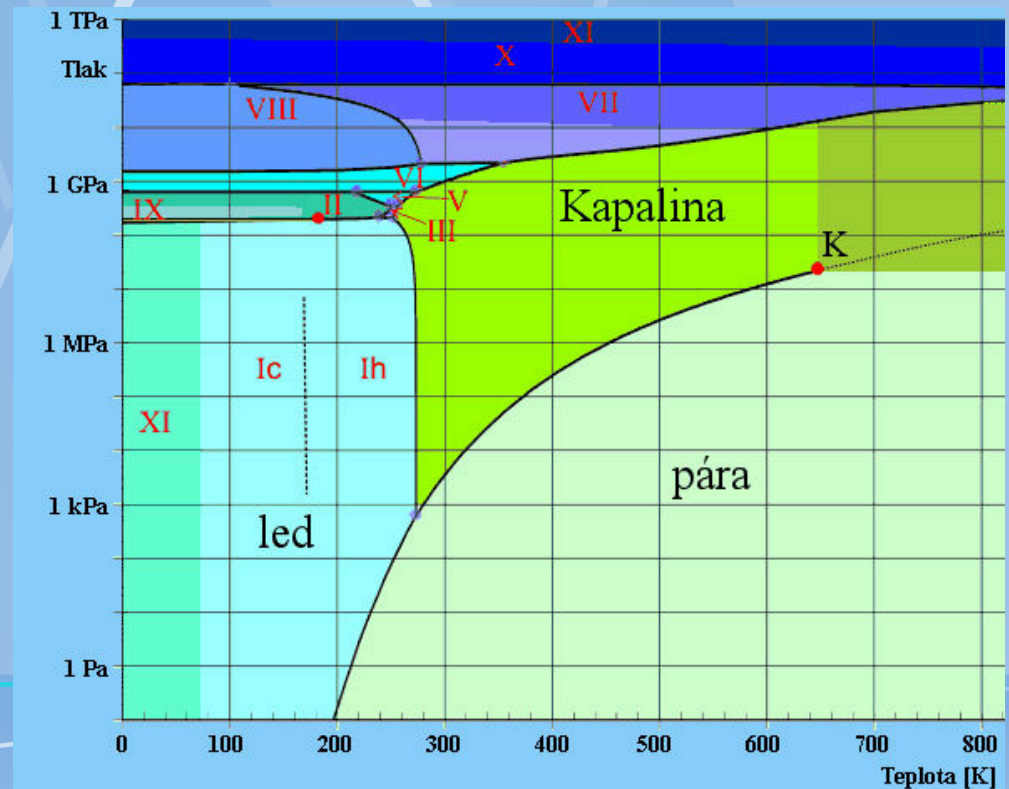
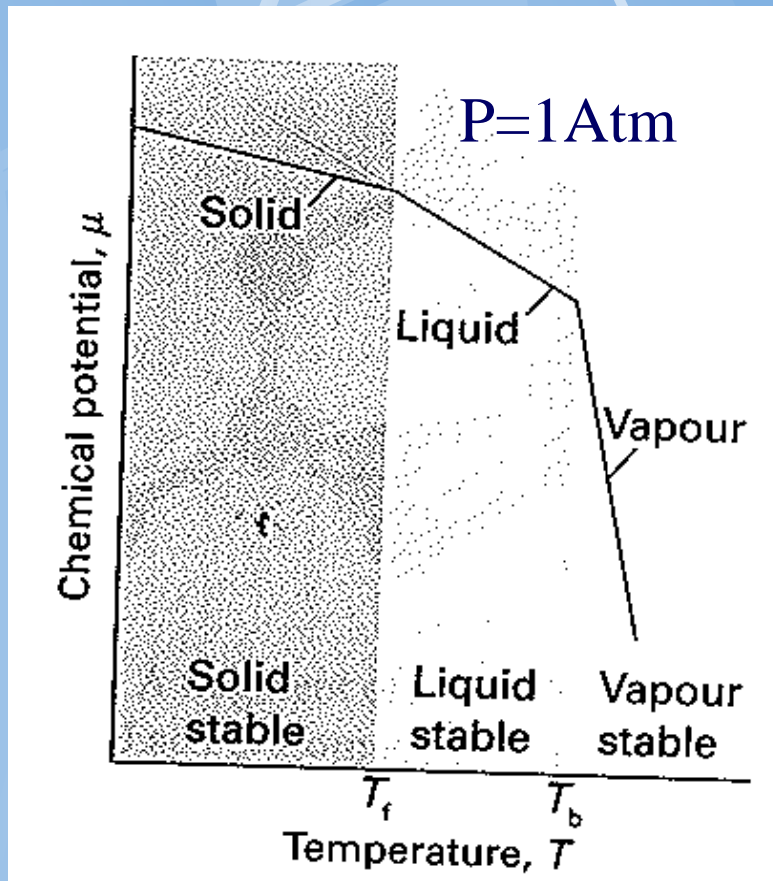
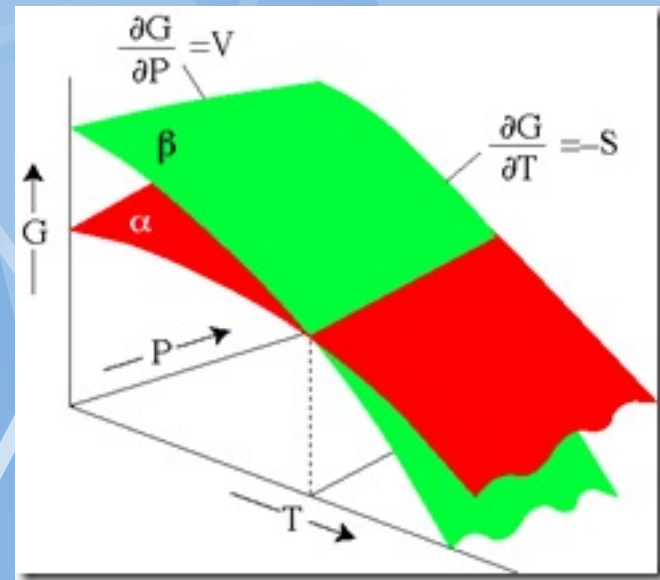
<http://academic.keystone.edu/jskinner/Limnology/AnomaliesOfWaterExplanations.htm>

http://www1.lsbu.ac.uk/water/thermodynamic_anomalies.html#fus

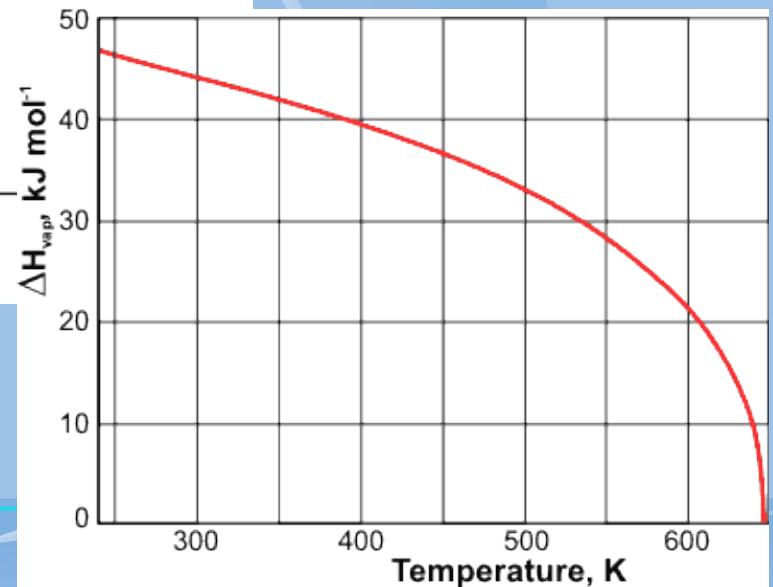
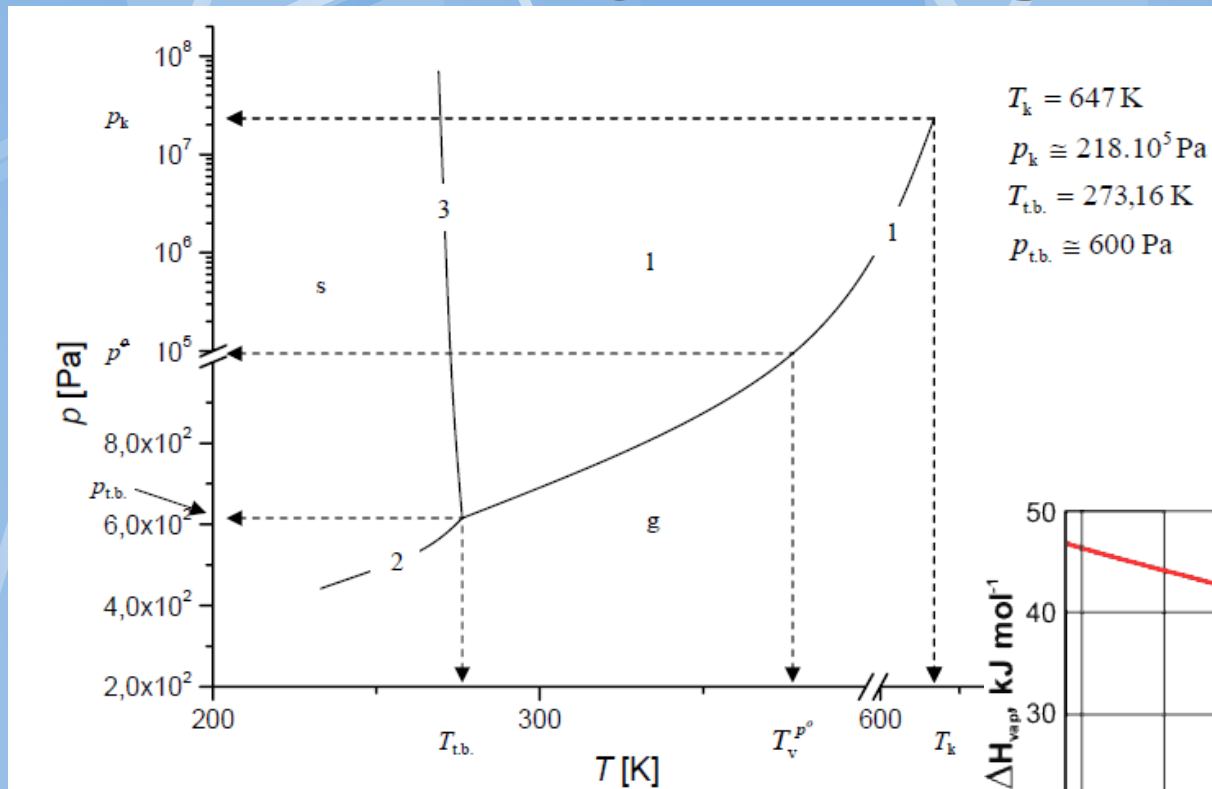
http://www1.lsbu.ac.uk/water/phase_anomalies.html

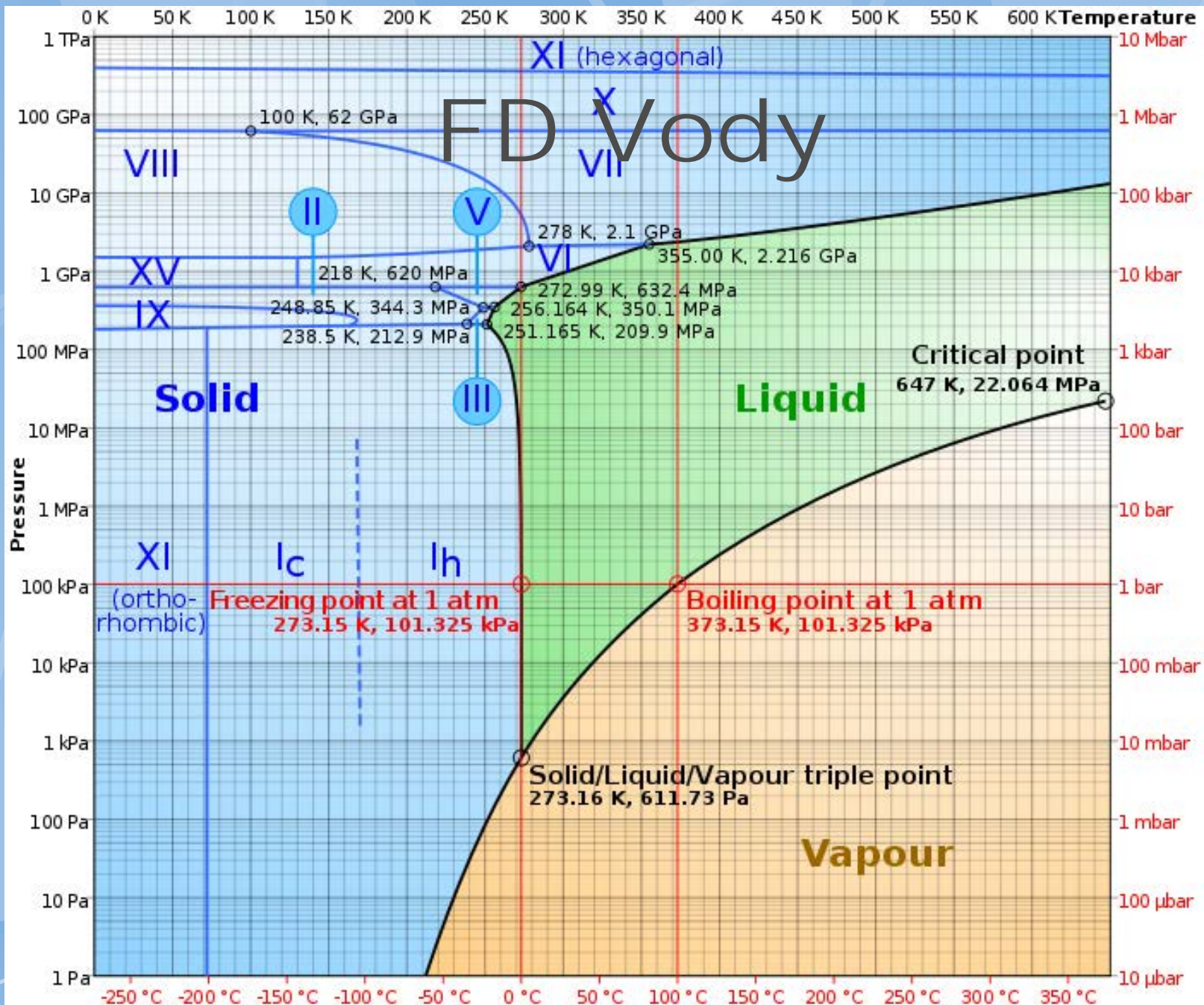


Gibbsova energie



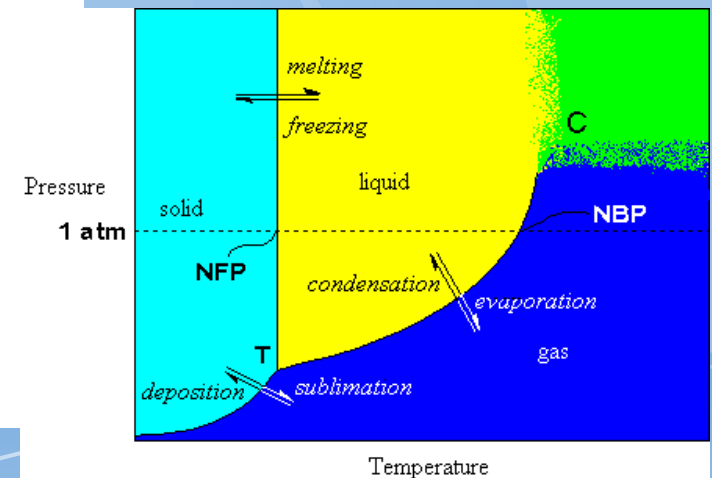
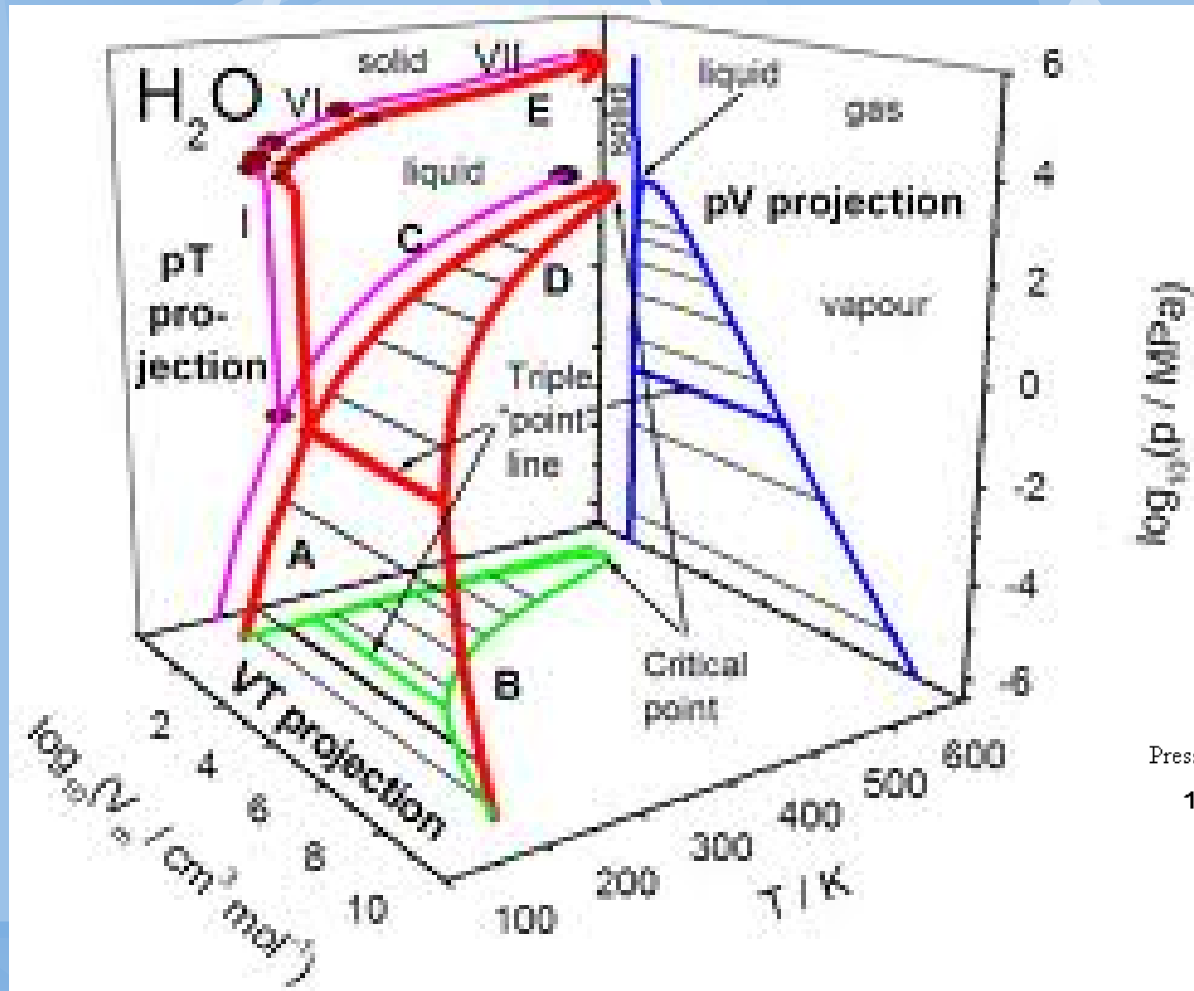
Kritický bod g-l vody



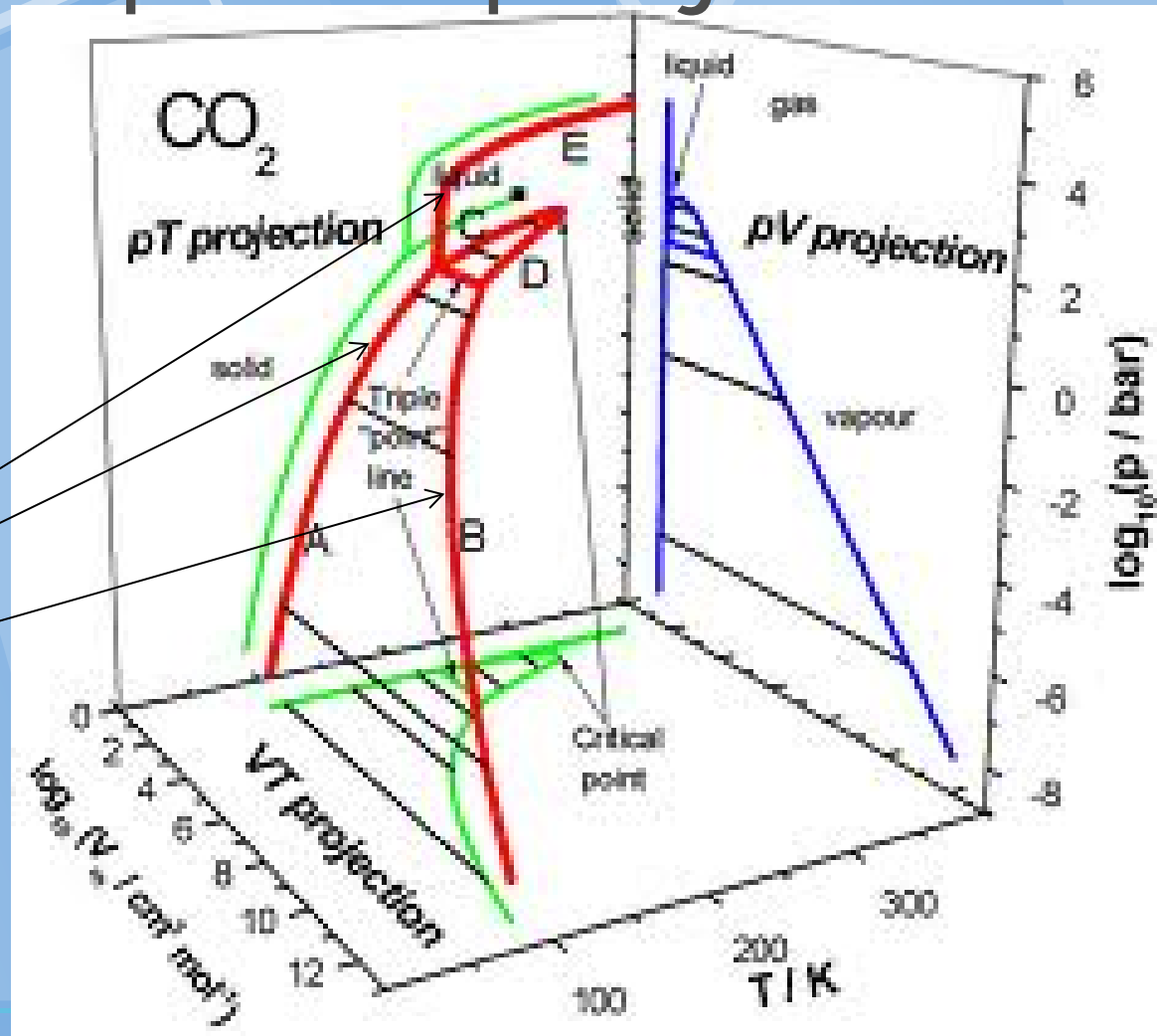


FD Vody

P-T-Vm projekce

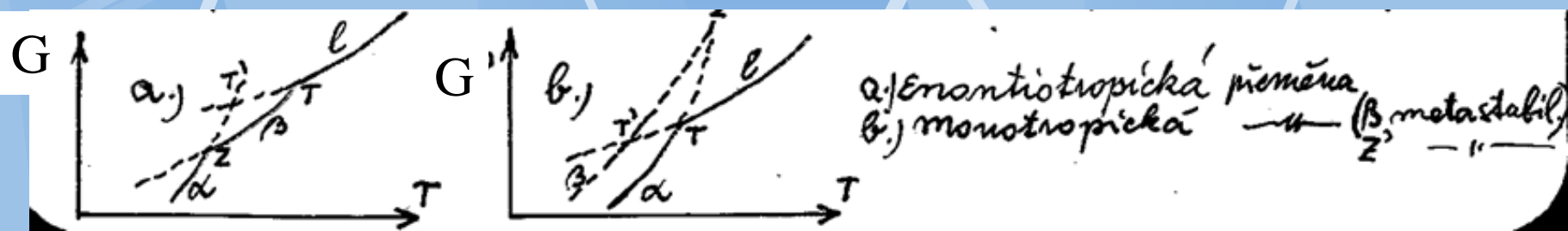


T-p-V_m projekce



Molární
objem
kapalně a
plynné fáze
(tuhá není
vynesena)

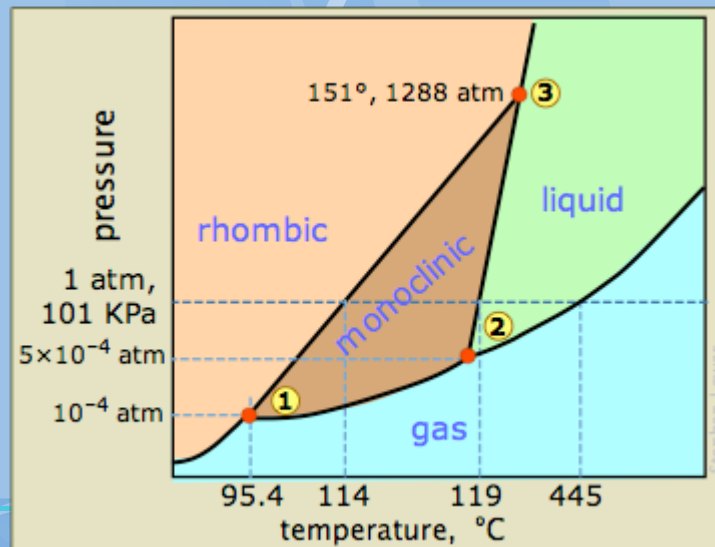
Nerovnovážné přeměny



Přeskočení fáze

Přeskočení na metastabilní fázi

Metastabilní FD síry:



http://chemwiki.ucdavis.edu/Wikitexts/Simon_Fraser_Chem1%3A_Lower/States_of_Matter/Changes_of_State

Diskuse

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

The heat of fusion of water with temperature exhibits a maximum at -17°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°C

The specific heat capacity (CP) has a maximum at about -45°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°C

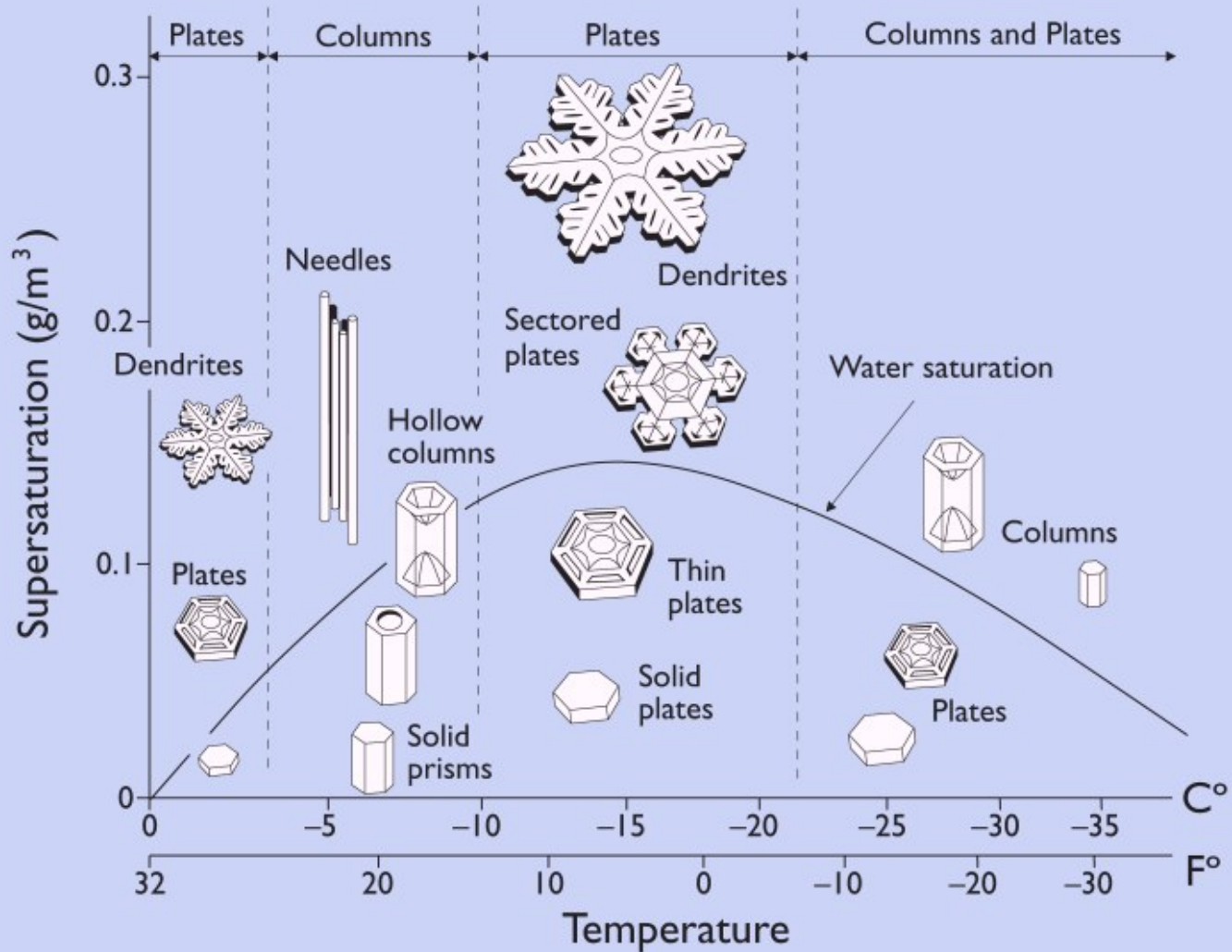
Voda



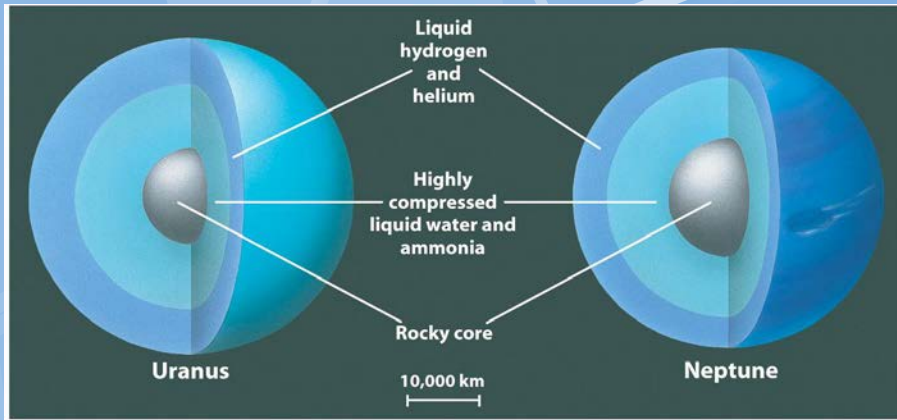
Out of the bosom of the Air,
Out of the cloud-folds of her garment shaken,
Over the woodlands brown and bare,
Over the harvest-field forsaken,
Silent, and soft, and slow
Descends the snow.

- Henry Wadsworth Longfellow (1807-1882)

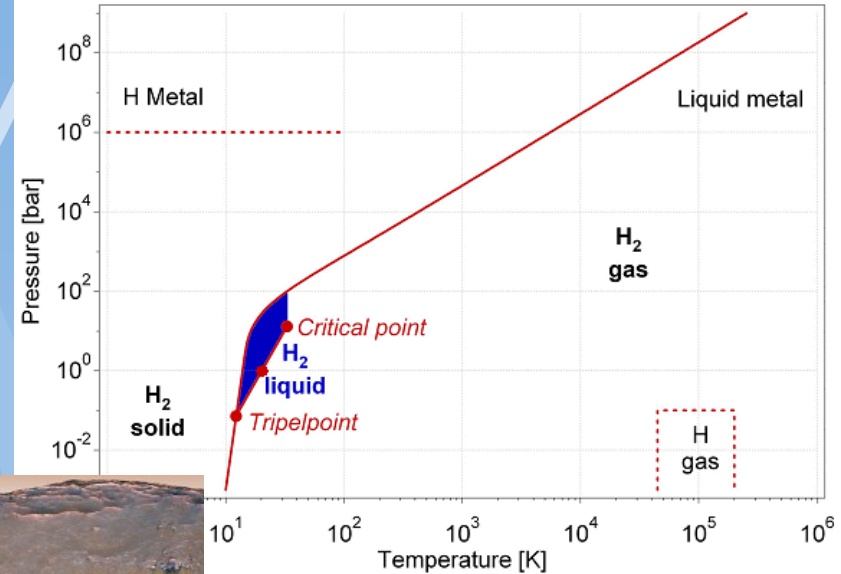
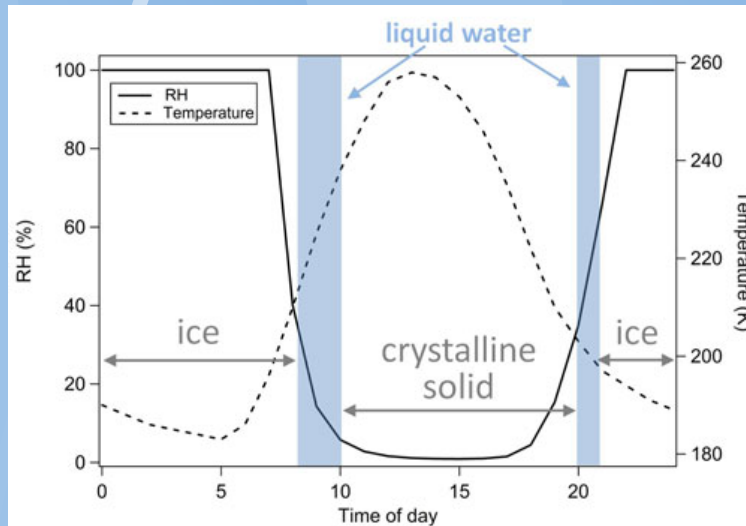
Diskuse



Fázové přeměny mimo Zemi



<http://www.astroblogs.nl/2015/06/23/vormt-zout-de-sleutel-tot-het-magnetisme-van-uranus-en-neptunus/>



Sodium perchlorate ($NaClO_4$)

<http://cires1.colorado.edu/science/groups/tolbert/people/gough/index.html>