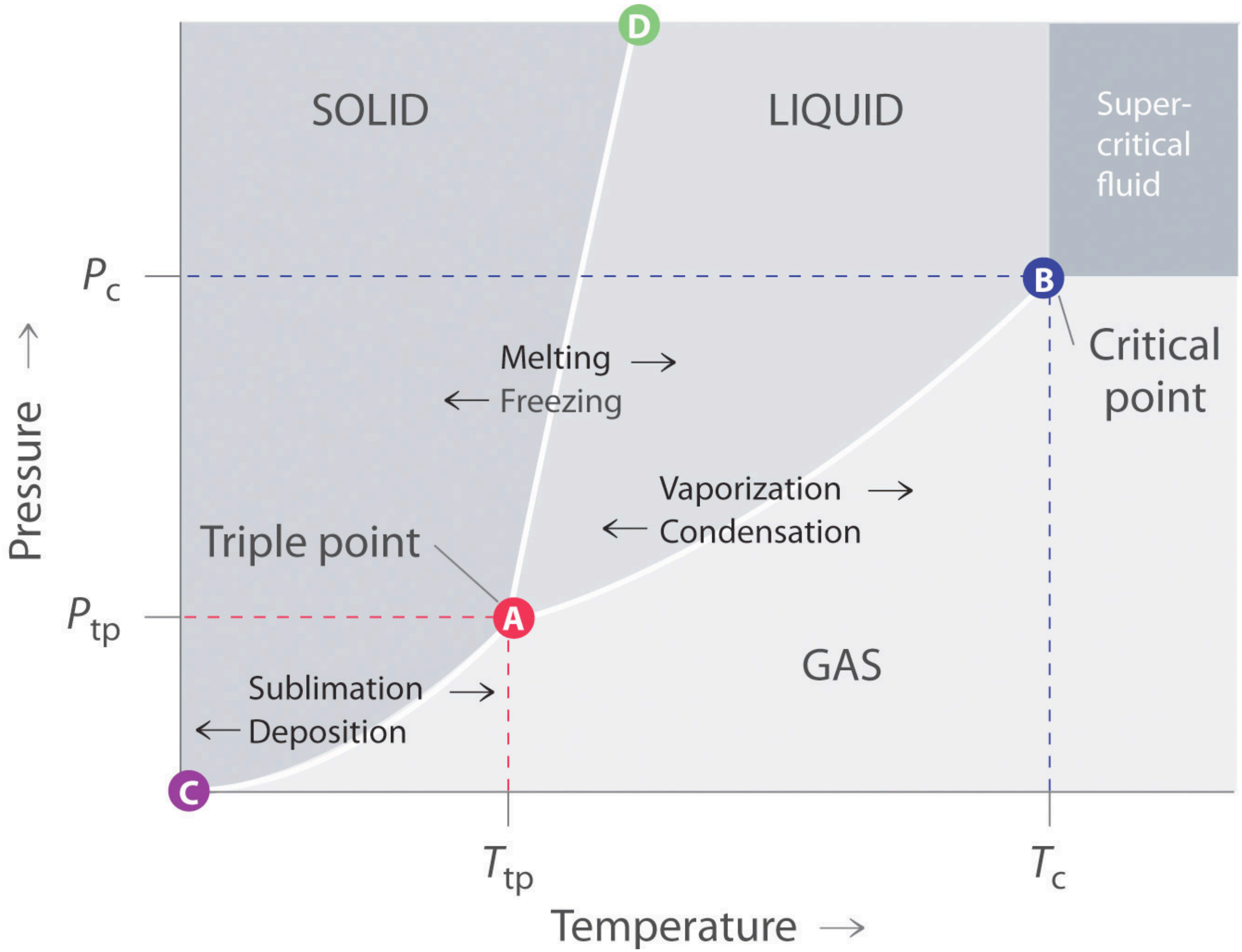
Faselikevekter, faseoverganger, fasediagram og tilstandsligninger

Fasediagram P-T



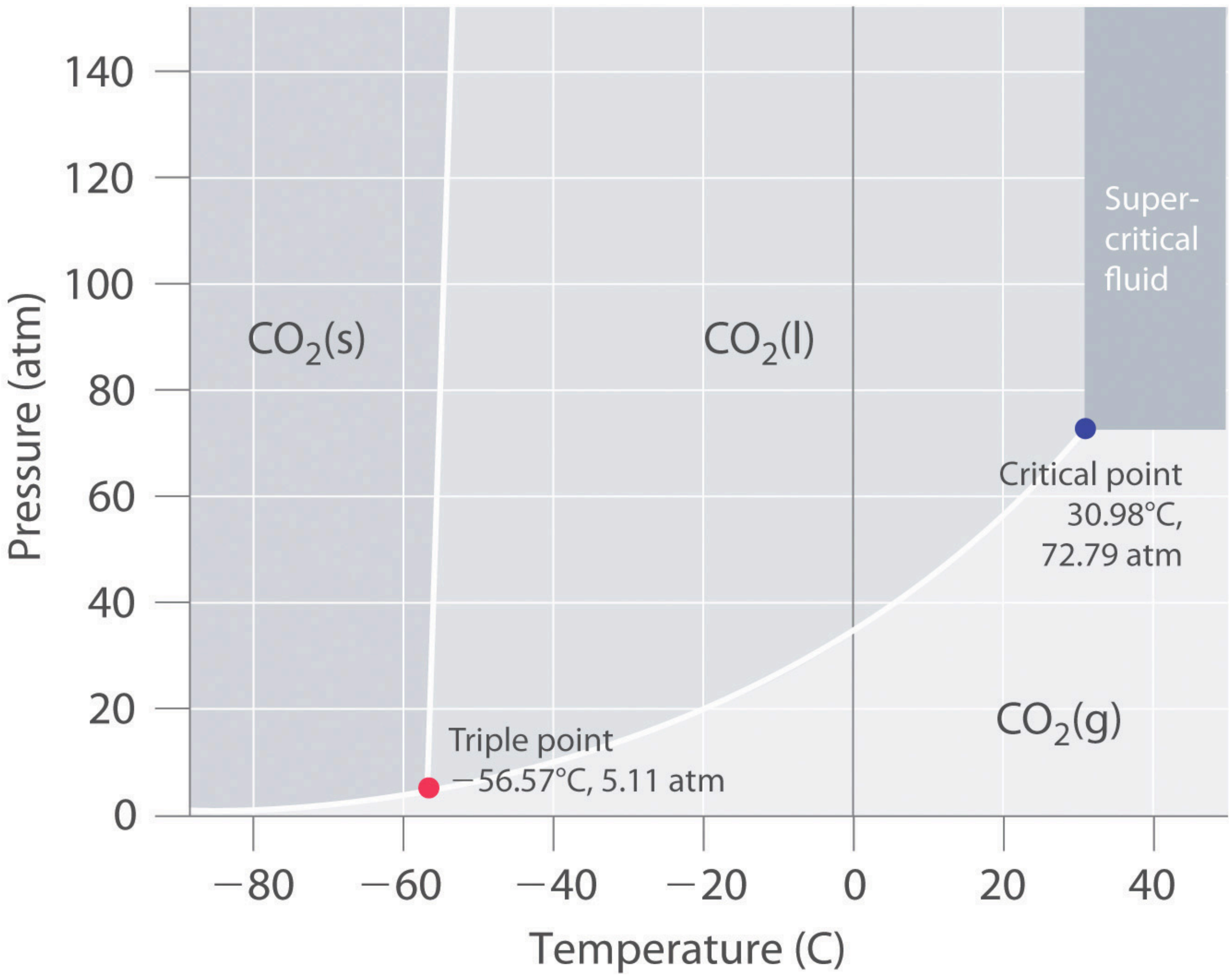
Koeksistenslinjer

A-C Fast stoff – gass

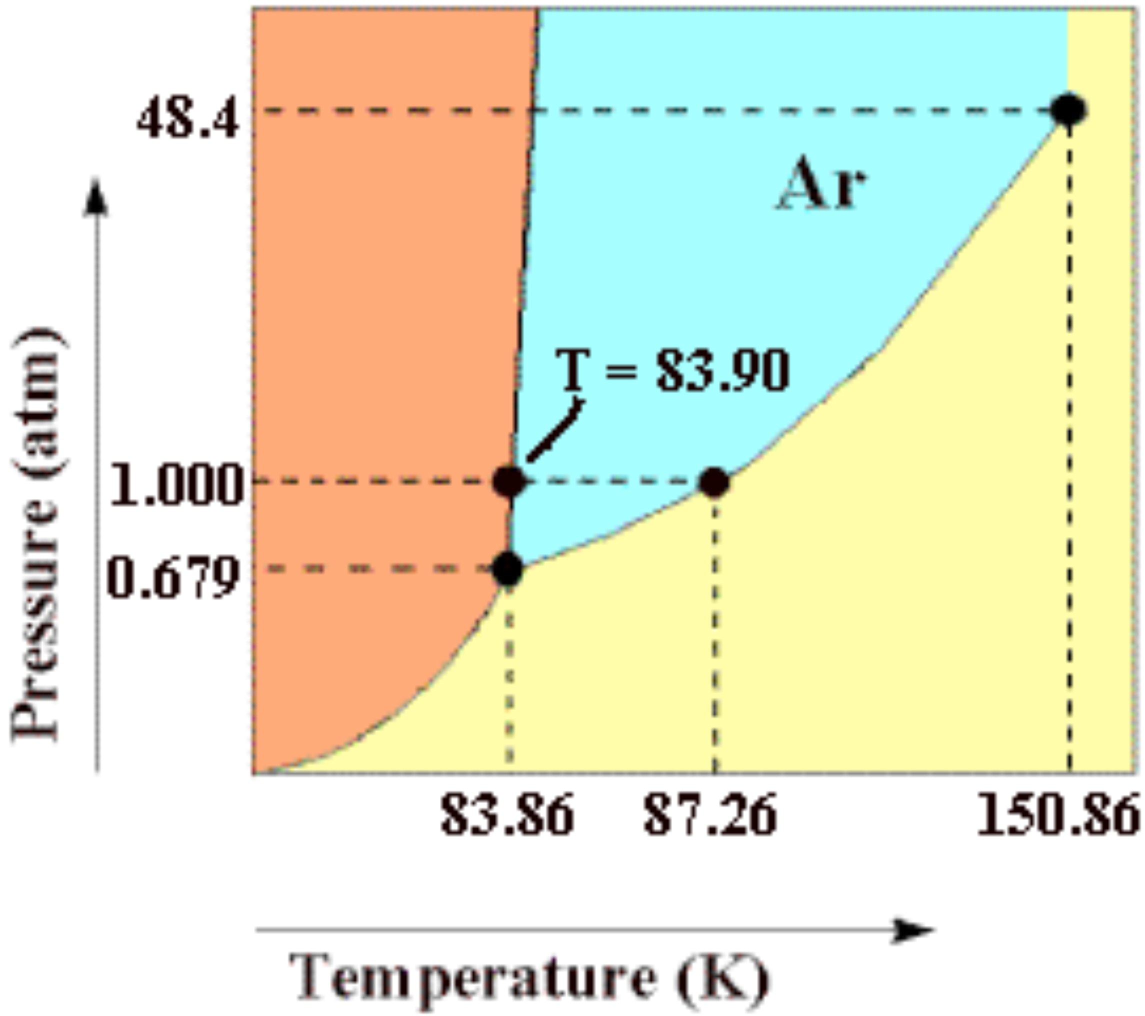
A-B Væske – gass

A-D Fast stoff – væske

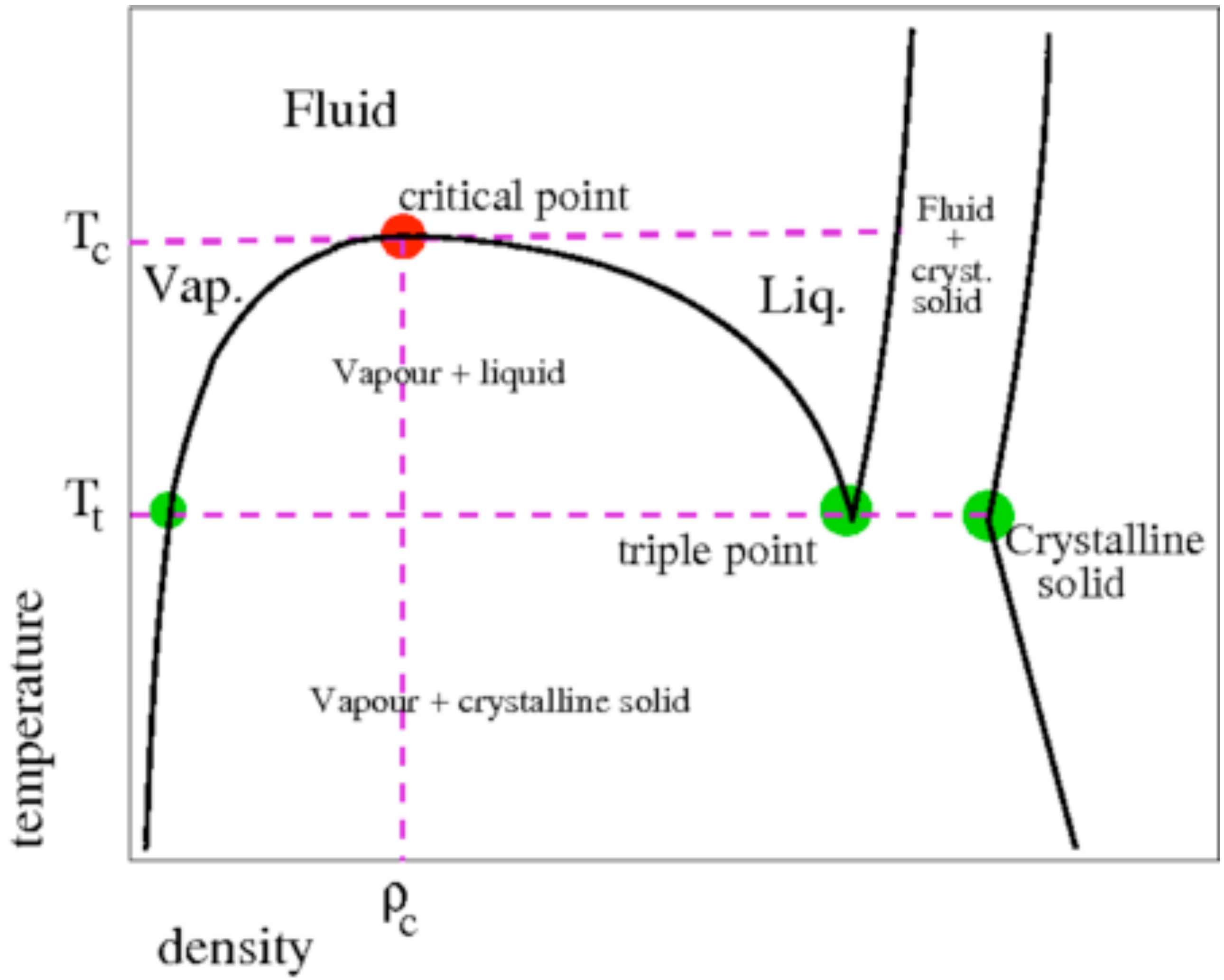
Fasediagram P-T for CO_2

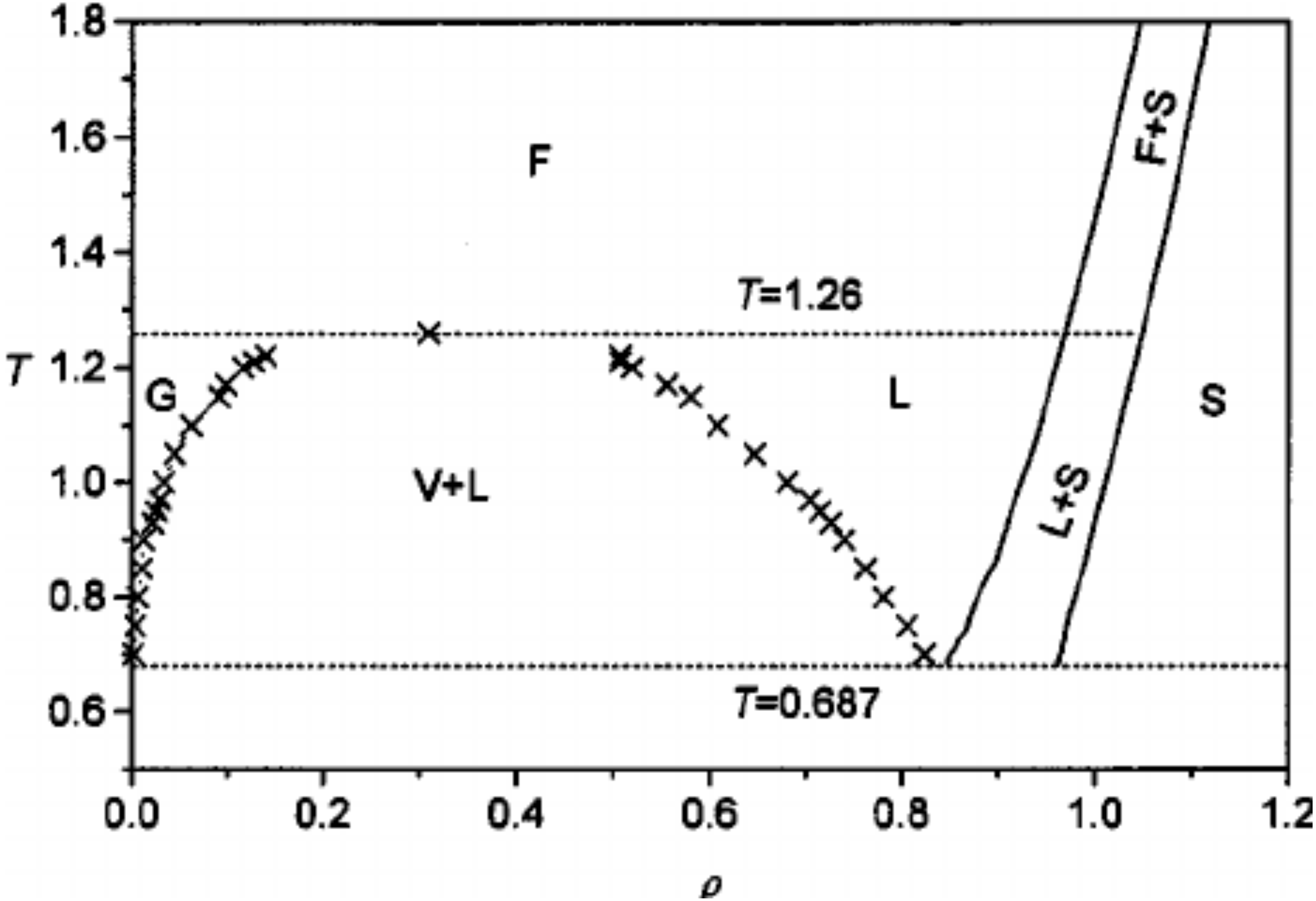


Fasediagram P-T, finn smelte- og fordampingstemperatur



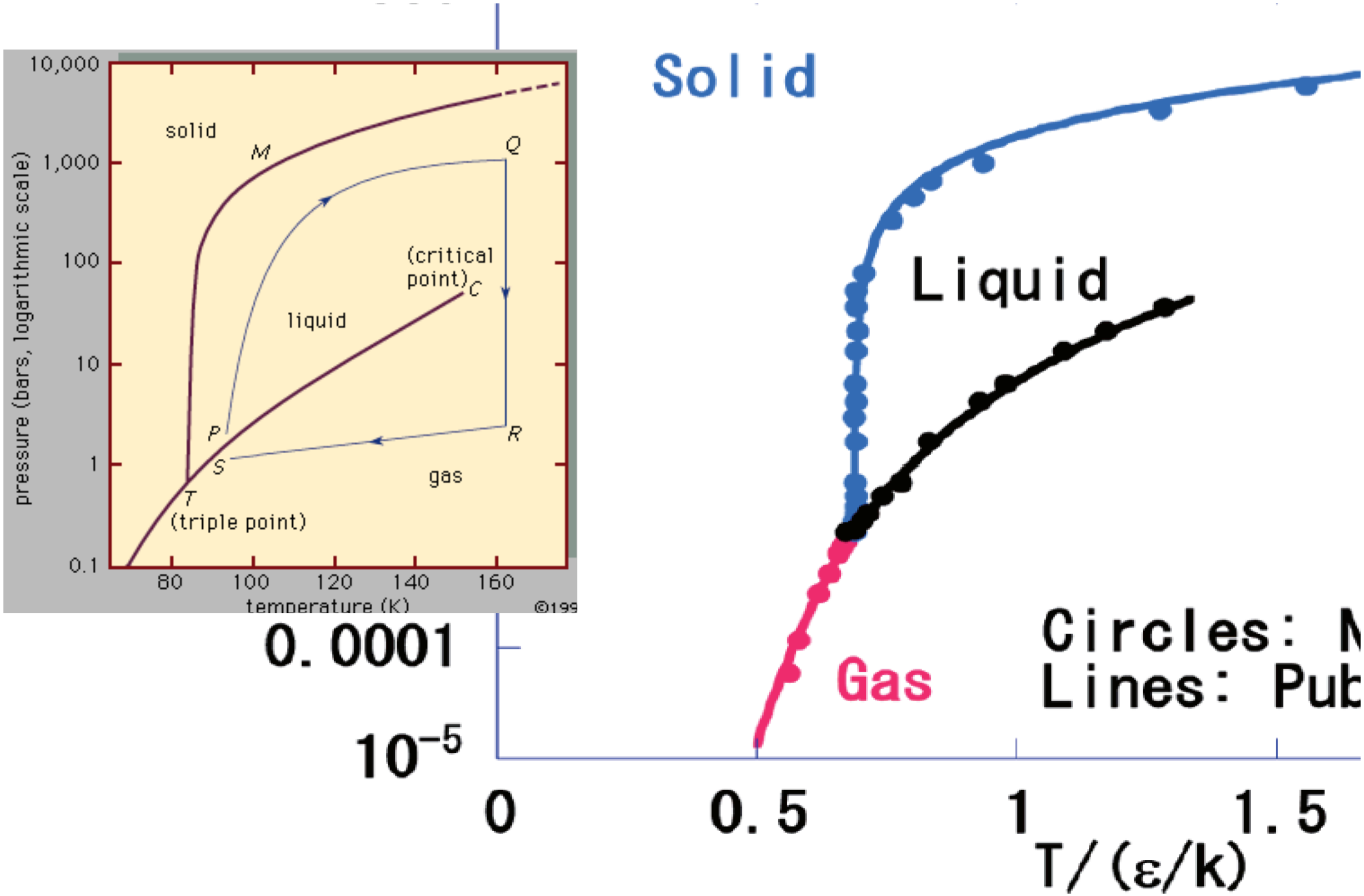
Fasediagram T-ρ





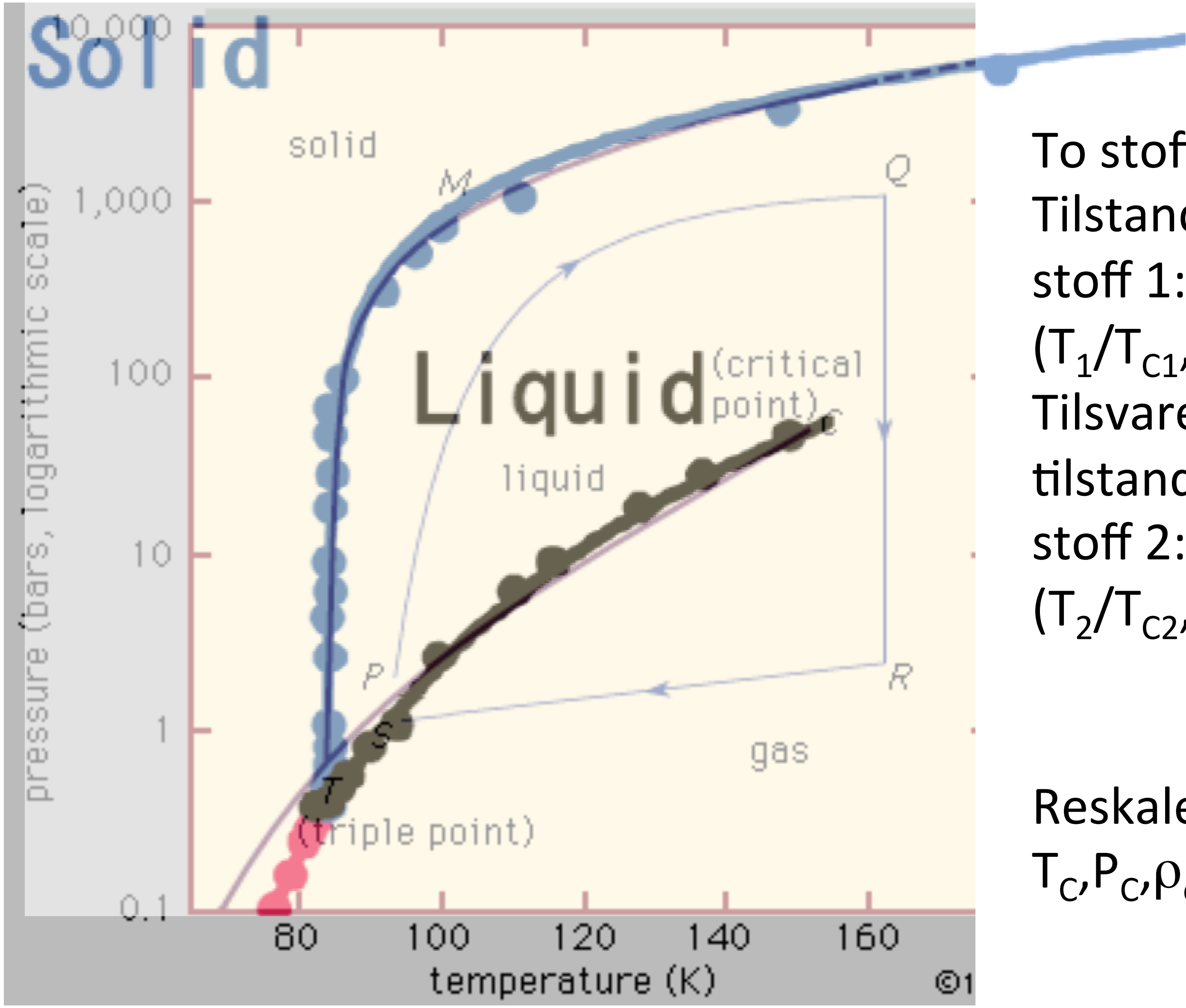
1.8
1.6
1.4
1.2
1.0
0.8
0.6
T
0.0
0.2
0.4
0.6
0.8
1.0
1.2
ρ
F
G
V+L
L
S
F+S
L+S
T=1.26
T=0.687

Lennard-Jones og Argon



”Loven” om tilsvarendede tilstander:

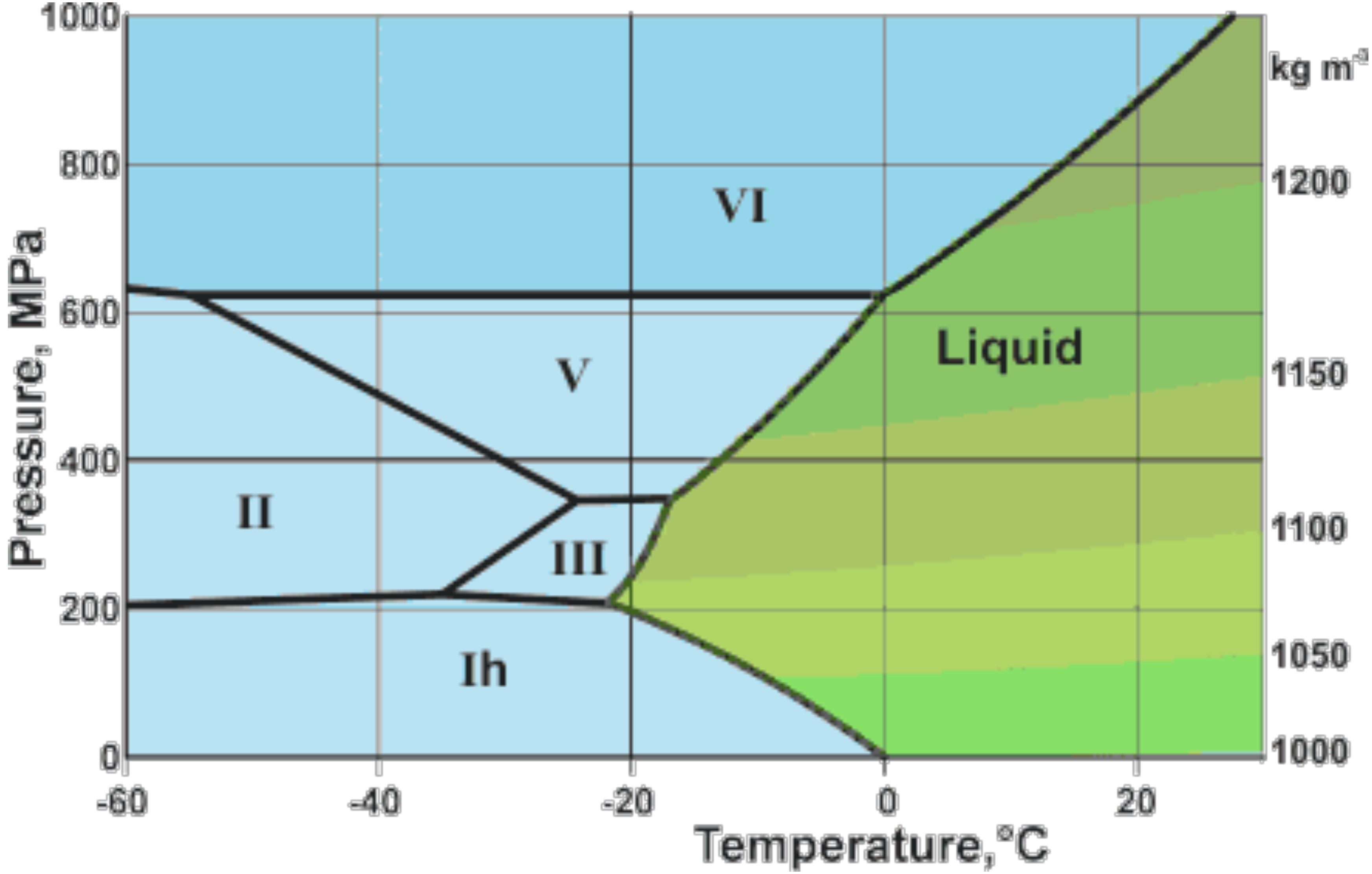
Lennard-Jones og Argon



To stoffer 1 og 2
Tilstanden for stoff 1:
$(T_1/T_{C1}, P_1/P_{C1})$
Tilsvarer tilstanden for stoff 2:
$(T_2/T_{C2}, P_2/P_{C2})$

Reskaler med
T_C, P_C, ρ_c

Mange faser: is



Kalsitt og Aragonitt

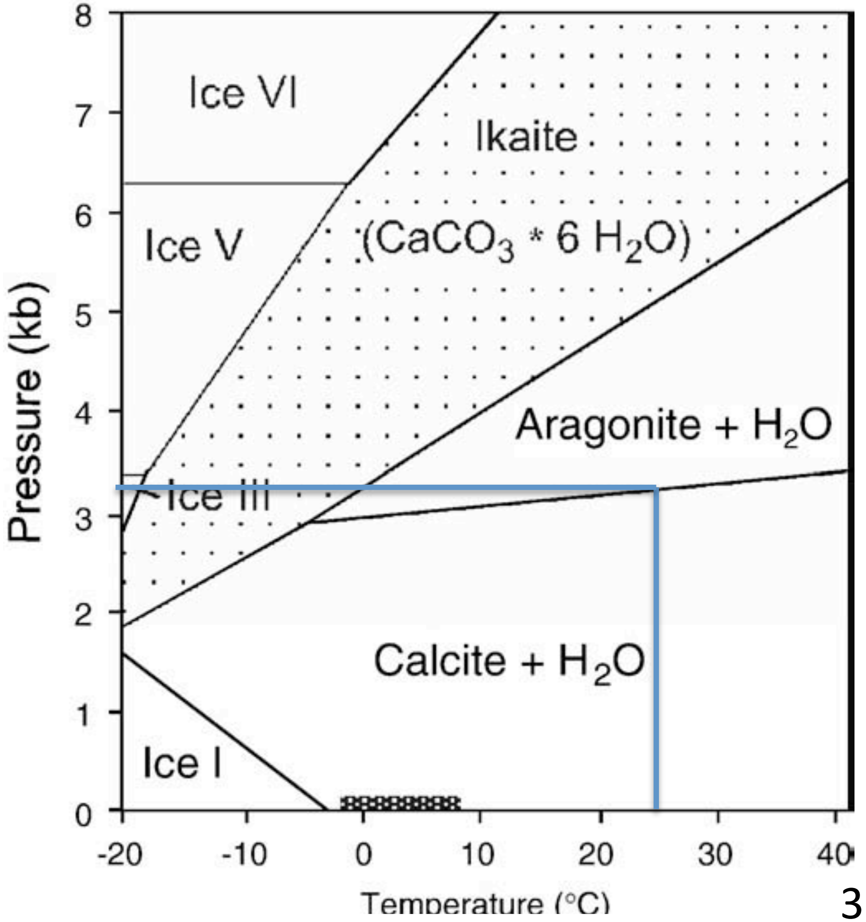
Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
Al (s)	0	0	28.33	24.35	9.99
Al_2SiO_5 (kyanite)	−2594.29	−2443.88	83.81	121.71	44.09
Al_2SiO_5 (andalusite)	−2590.27	−2442.66	93.22	122.72	51.53
Al_2SiO_5 (sillimanite)	−2587.76	−2440.99	96.11	124.52	49.90
Ar (g)					
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)					3.42
CH_4 (g)					
C_2H_6 (g)					
C_3H_8 (g)					
C_2H_5OH (l)					58.4
$C_6H_{12}O_6$ (gl					
CO (g)					
CO_2 (g)					
H_2CO_3 (aq)					
HCO_3^- (aq)	−691.99	−586.77	91.2		
Ca^{2+} (aq)	−542.83	−553.58	−53.1		
$CaCO_3$ (calcite)	−1206.9	−1128.8	92.9	81.88	36.93
$CaCO_3$ (aragonite)	−1207.1	−1127.8	88.7	81.25	34.15
$CaCl_2$ (s)	−795.8	−748.1	104.6	72.59	51.6

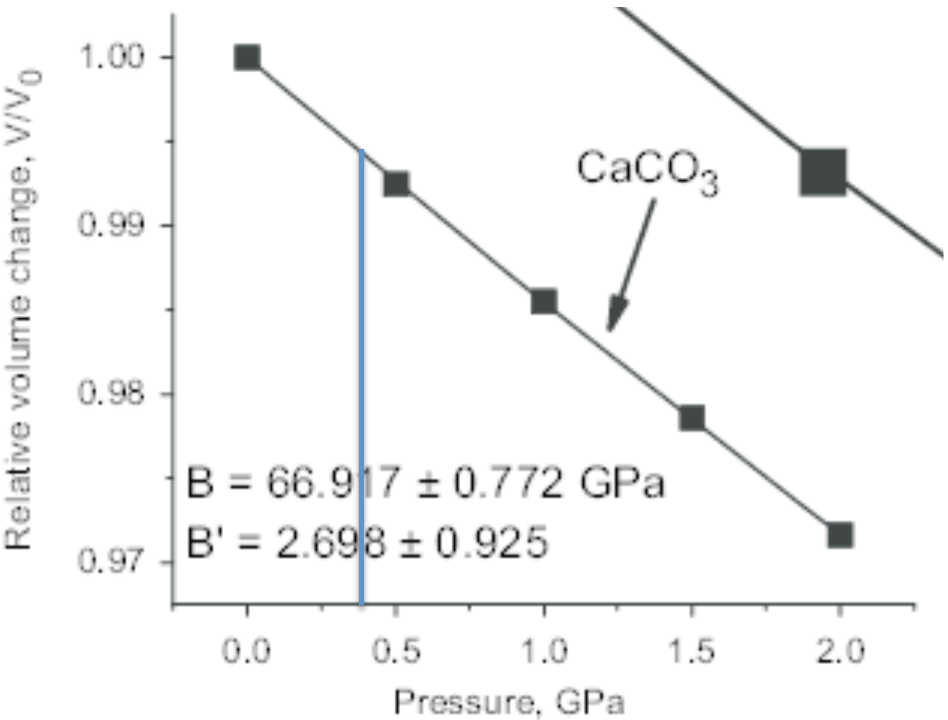
Er kalsitt eller aragonitt stabil ved 25C og 1 atmosfære?

Ved hvilket trykk er aragonitt stabilt?

- $\Delta_f G_K - \Delta_f G_A = \Delta(TS) < 0$
- $\Delta_f G_K - \Delta_f G_A = -1$ kJ/mol
- $dG = VdP - SdT + \mu dN$
- $\Delta G_K - \Delta G_A = (V_K - V_A)\Delta P$
- $\Delta_f G_K - \Delta_f G_A + \Delta G_K - \Delta G_A = 10^3 + 2.78*10^{-6}\ \Delta P = 0$
- $\Delta P = 360$ MPa

Kalsitt og aragonitt





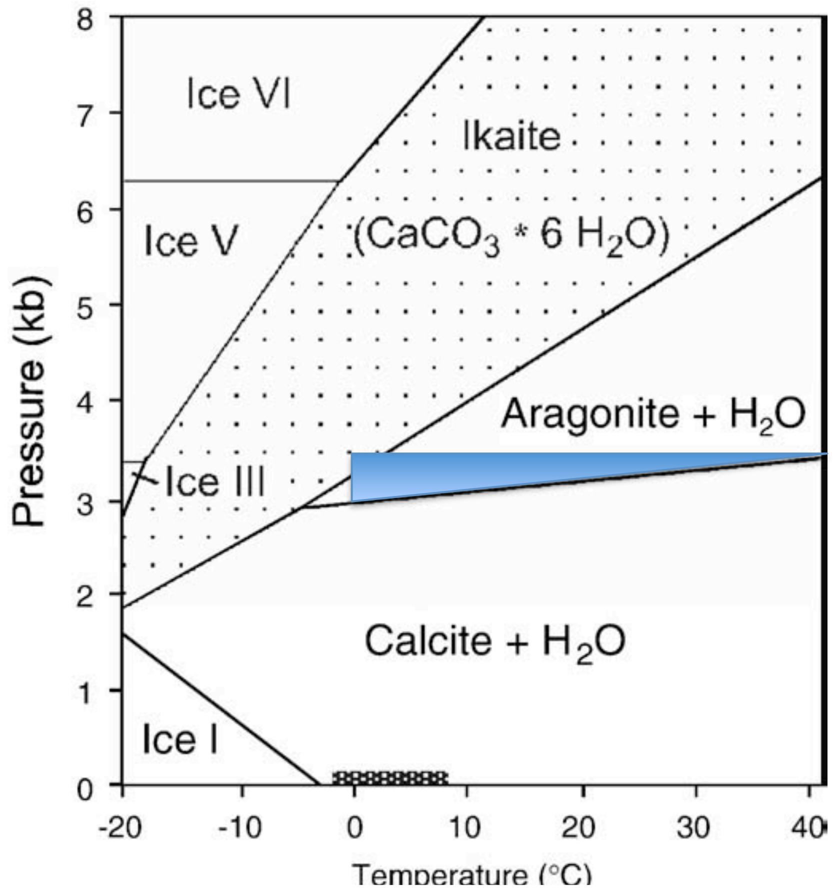
360 MPa = 0.36 GPa = 3.6 kbar

Tetthet jordskorpe 2600kg/m^3, => z = - p/(rg) = 14km

Clausius-Clapeyrons relasjon

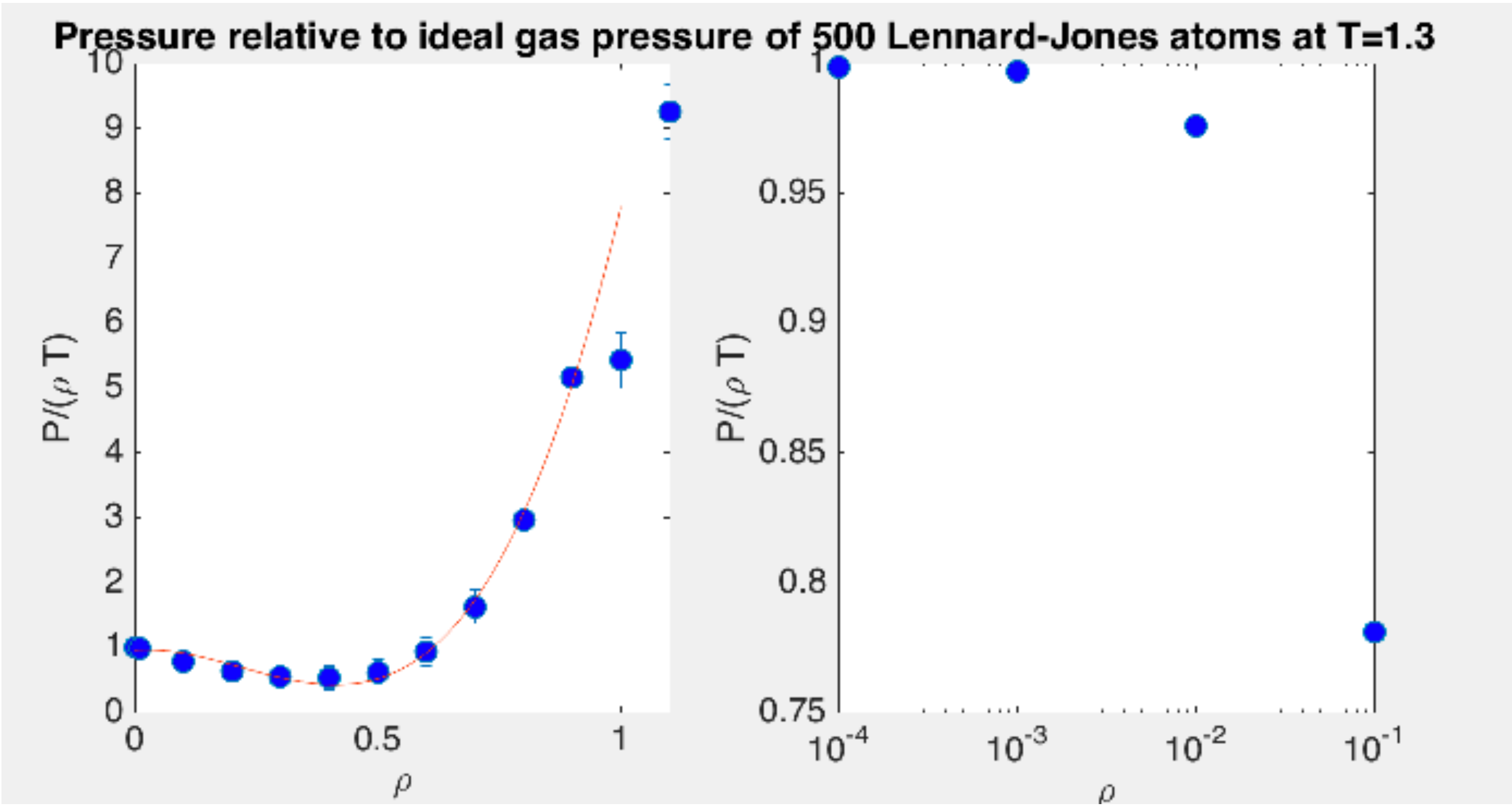
- dG = VdP − SdT
- => Formen til en fasegrense i PT-diagram er gitt av V og S
- $G_A = G_B$ på fasegrenselinjen
- $dG_A = dG_B$ for å forbli på linjen
- $-S_A dT+V_A dP=-S_B dT+V_B dP$

- => $dP/dT = (S_A-S_B)/(V_A-V_B) = \Delta s/\Delta v$
- $dP/dT = \Delta h/(T\ \Delta v) = L/(T\ \Delta V)$
- ΔS = 92.9-88.7 J/K = 4.2 J/K
- ΔV = 36.93-34.15 cm^3 = 2.8 cm^3
- dP/dT = 1.5 MPa/K = 0.015 kb/K = 0.6 kb/ 40 K



Tilstandsligninger

- **Ideell gass**: PV=NkT, $P^*=\rho^*T^*$
- **Virial-ligningen:** $P^*/(\rho^*T^*) = 1 + \rho + \rho^2 + \rho^3 + \ldots$



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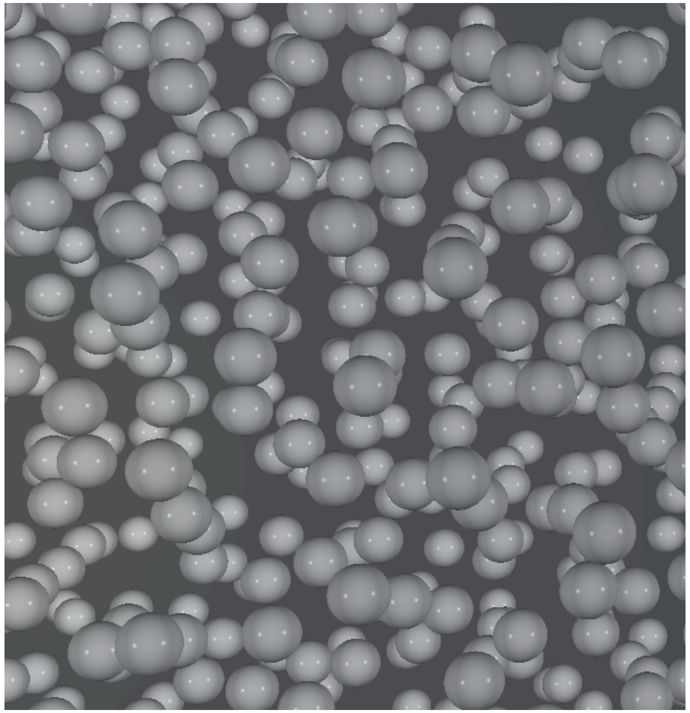
- **Clausius:** P (V-Nb) = NkT
- Nb: minste mulige volum
- b ~ molekyldiameter^3 ~ $V_c/(3N)$ ~ $2\sigma^3$



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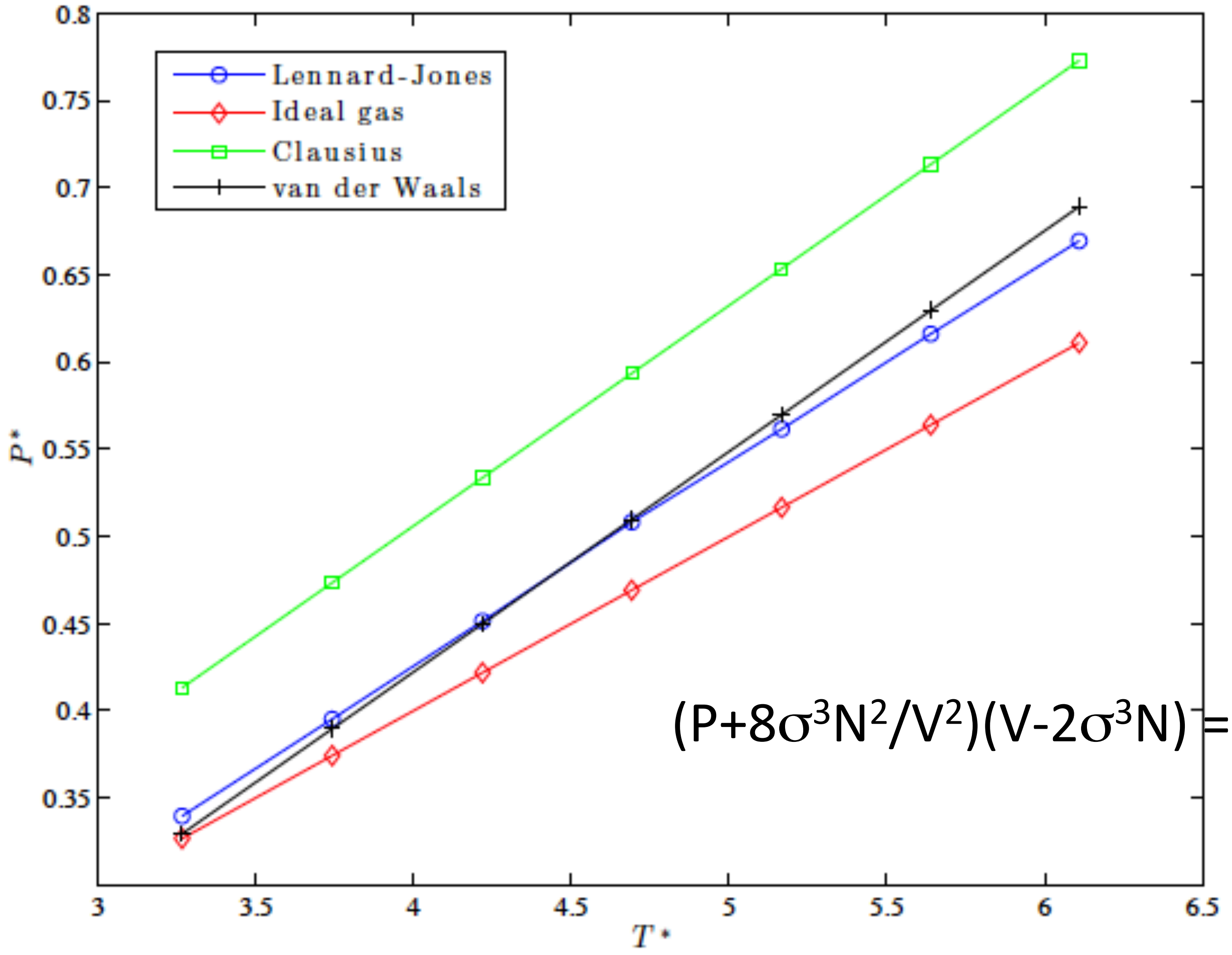
- **van der Waals:** $(P+aN^2/V^2)(V-Nb) = NkT$
- aN^2/V^2:
  - potensiell energi til ett molekyl U~N/V
  - potensiell energi til alle molekyl $U \sim N^2/V$
  - Trykk $P = dU/dV = - aN^2/V^2$
- $a \sim 3p_cv_c^2 \sim 8\sigma^3$



$$(P+8\sigma^3N^2/V^2)(V-2\sigma^3N) = NkT$$

- $T' = T/T_c$, $P = P/P_c$, $V = V/V_c$
- vdW: $(p'+3/V'^2)(V'-1/3) = 8T'/3$