Single Component Systems

First Order Transition

Gibbs Free Energy is the same for water and ice at 0°C. Slope is different, ΔS.
There is an enthalpy of fusion ΔH_f and an entropy change on melting ΔS_f.
These balance $\Delta G = \Delta H - T\Delta S = 0$.
$C_p = (\partial H/\partial T)_p$ There is a change in the slope of the H vs. T plot at the melting point. Ice holds less heat than water.

$$\Delta G_f = 0 = \Delta H_f - T_f \Delta S_f$$
$$T_f = \Delta H_f/\Delta S_f$$

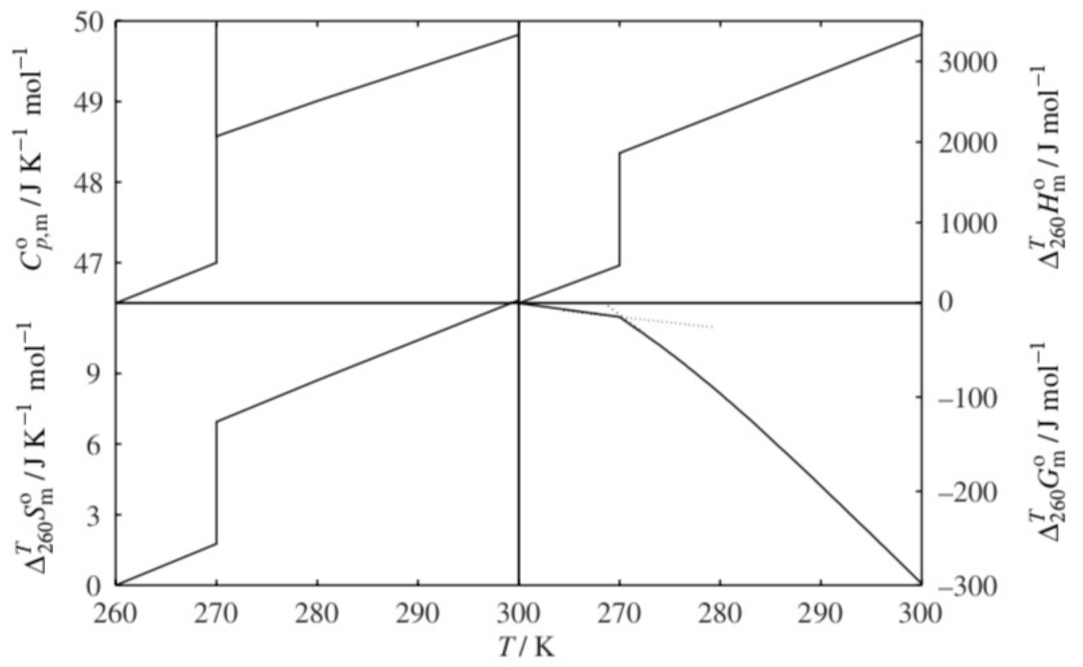


Figure 2.1 The temperature variation of the heat capacity, enthalpy, entropy, and Gibbs energy close to the first-order semiconductor to metal transition in NiS [1].

Mott Transition

https://en.wikipedia.org/wiki/Mott_transition

Second Order Transition

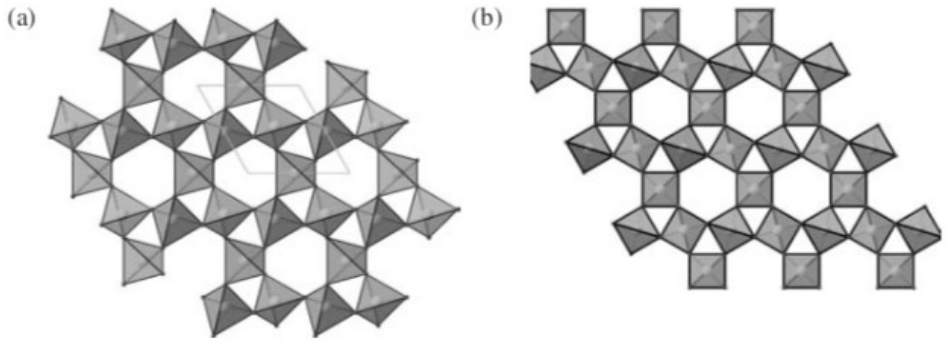


Figure 2.2 Crystal structure of α- (low) and β- (high) quartz (SiO_2).

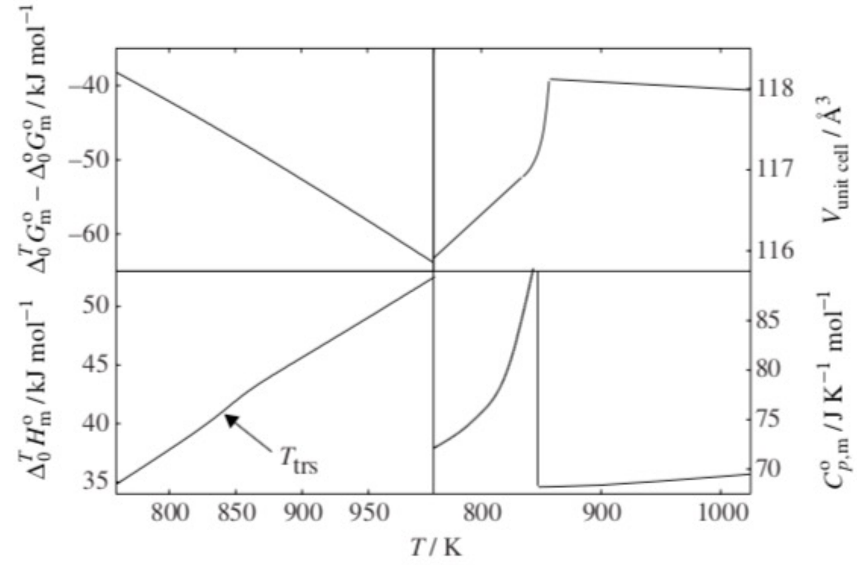


Figure 2.3 The temperature variation of the Gibbs energy [5], unit-cell volume [4] enthalpy and heat capacity [5] at the second-order α- to β-quartz transition of SiO_2. Second-order derivatives of the Gibbs energy like the heat capacity have discontinuities at the transition temperature.

Clausius-Clapeyron Equation
(what is the dependence of vapor pressure on temperature?)

Consider two phases at equilibrium, α and β

-S U V
H A
-p G T

$d\mu_\alpha = d\mu_\beta$

$dG = Vdp - SdT$
$d\mu_\alpha = d\mu_\beta$
So,
$V^\alpha dp - S^\alpha dT = V^\beta dp - S^\beta dT$
So,
$dp/dT = \Delta S/\Delta V$
and
$\Delta G = 0 = \Delta H - T_{trans}\Delta S$ so $\Delta S = \Delta H/T_{trans}$
and
$\mathbf{dp/dT = \Delta H/(T_{trans}\Delta V)}$ Clapeyron Equation
For transition to a gas phase, $\Delta V \sim V^{gas}$
and for low density gas (ideal) $V = RT/p$
$\mathbf{d(\ln p_{vap})/dT = \Delta H_{vap}/(RT_{vap}^2)}$ Clausius-Clapeyron Equation

This allows calculation of the vapor pressure as a function of T

Clausius Clapeyron Equation

$d(\ln p^{Sat})/dT = \Delta H_{vap}/(RT_{vap}^2)$ Clausius-Clapeyron Equation

$d(\ln p^{Sat}) = (-\Delta H_{vap}/R)\, d(1/T)$

$\ln[p^{Sat}/ p_C^{Sat}] = (-\Delta H_{vap}/R)\, [1/T - 1/T_C]$ Use the critical point as the reference state

Shortcut Vapor Pressure Calculation:

$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right)$$

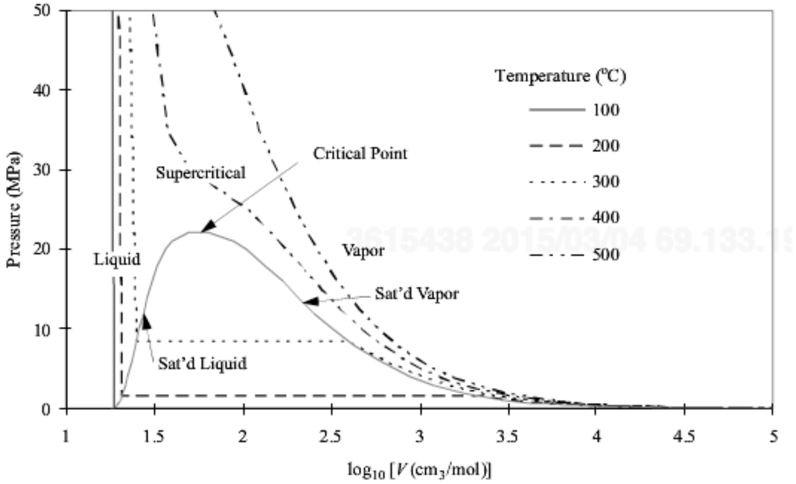


Figure 1.4 *P-V-T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.*

From the "Chemical Engineering Book" Elliot and Lira

Clausius Clapeyron Equation

$d(\ln p^{Sat}) = (-\Delta H_{vap}/R)\, d(1/T)$

$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right)$$

$\ln[p^{Sat}/ p_R^{Sat}] = (-\Delta H_{vap}/R)\, [1/T - 1/T_R]$

This is a kind of Arrhenius Plot

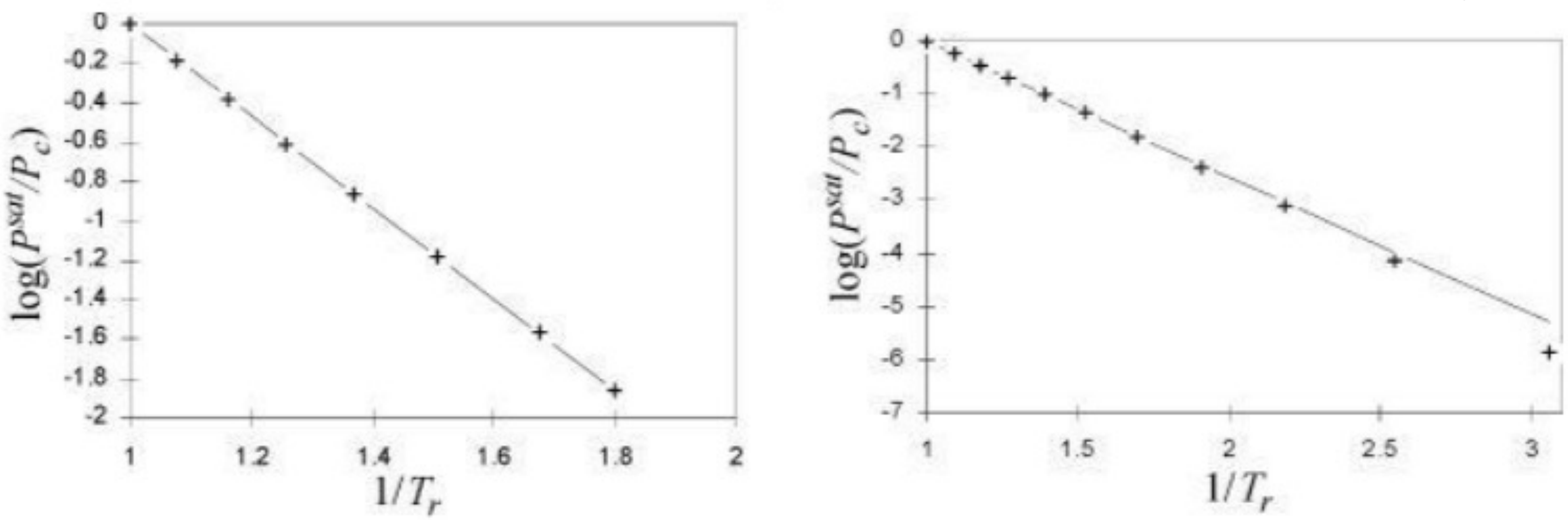


Figure 9.1. Plot to evaluate Clausius-Clapeyron for calculation of vapor pressures at high pressures, argon (left) and ethane (right).

Clausius Clapeyron Equation

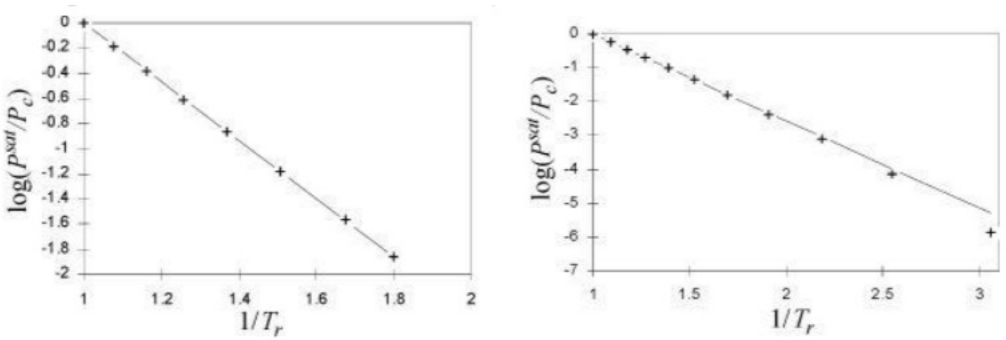


Figure 9.1. Plot to evaluate Clausius-Clapeyron for calculation of vapor pressures at high pressures, argon (left) and ethane (right).

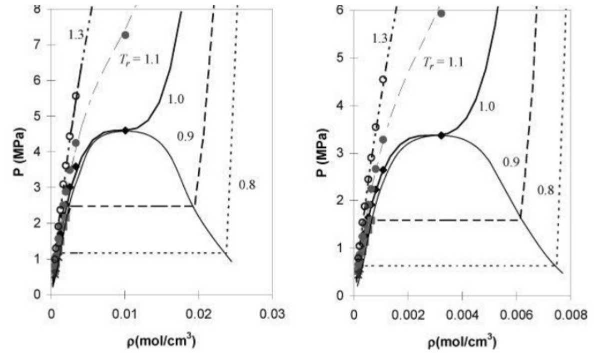


Figure 7.1. Comparison of the PρT behavior of methane (left) and pentane (right) demonstrating the qualitative similarity which led to corresponding states' treatment of fluids. The lines are calculated with the Peng-Robinson equation to be discussed later. The phase envelope is an approximation sketched through the points available in the plots. The smoothed experimental data are from Brown, G.G., Sounders Jr., M., and Smith, R.L., 1932. Ind. Eng. Chem., *24*:513. Although not shown, the Peng-Robinson equation is not particularly accurate for modeling liquid densities.

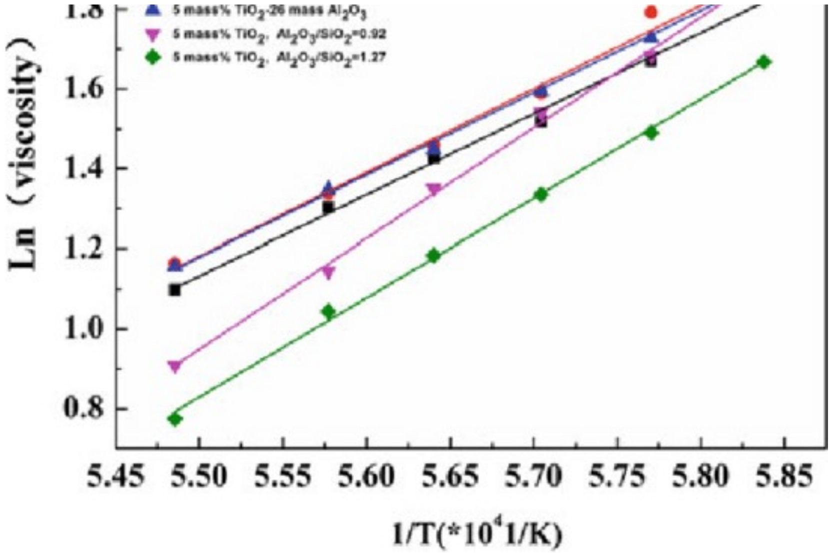
“A” Not dependent on T for Arrhenius

$$\mu = Ae^{B/T}$$

This is a kind of Arrhenius Plot

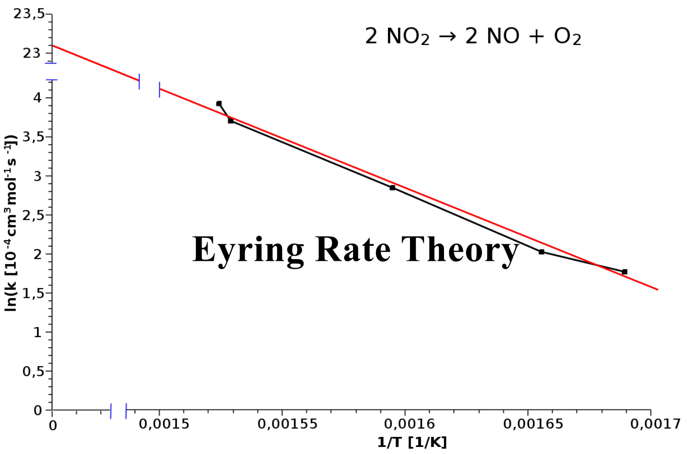
$$V(t) = V_0 e^{-\frac{t}{RC}},$$

The constant $\tau = RC$



$$k = Ae^{\frac{-E_a}{RT}}$$

A ~ kT/h for Eyring



Eyring Rate Theory

Both Eyring and Arrhenius are “rate” laws not equilibrium laws

$d(\ln p^{Sat}) = (-\Delta H_{vap}/R)\ d(1/T)$

$\ln[p^{Sat}/\ p_R^{Sat}] = (-\Delta H_{vap}/R)\ [1/T - 1/T_R]$

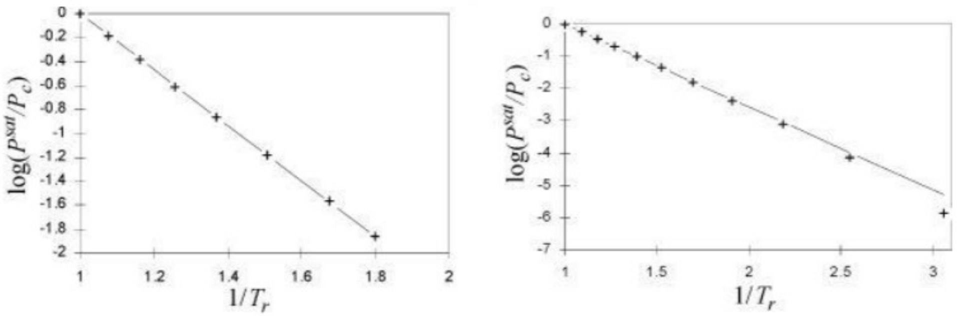


Figure 9.1. Plot to evaluate Clausius-Clapeyron for calculation of vapor pressures at high pressures, argon (left) and ethane (right).

Clapeyron Equation predicts linear T vs p for transition

$dp/dT = \Delta H/(T\Delta V)$
Clapeyron Equation

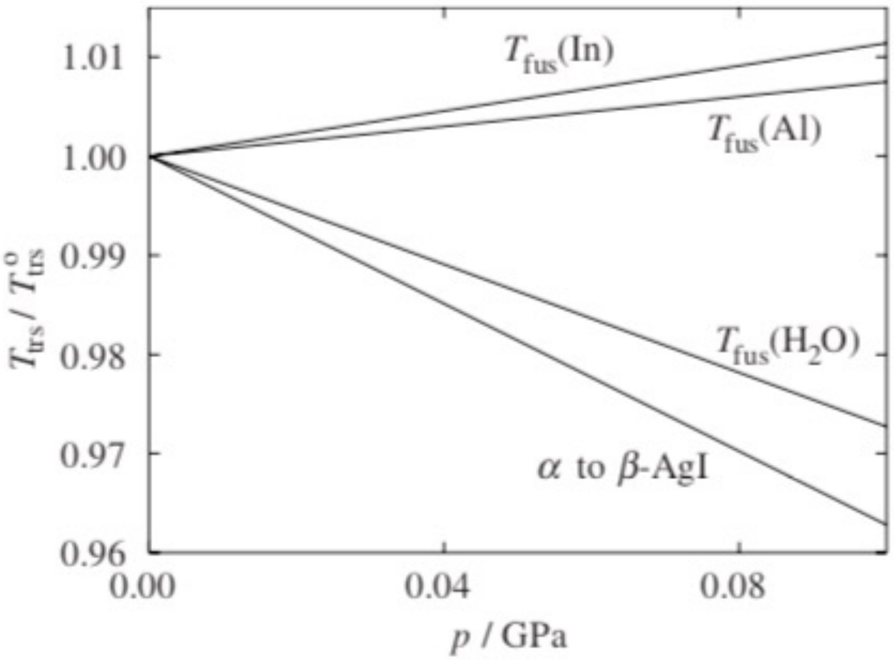
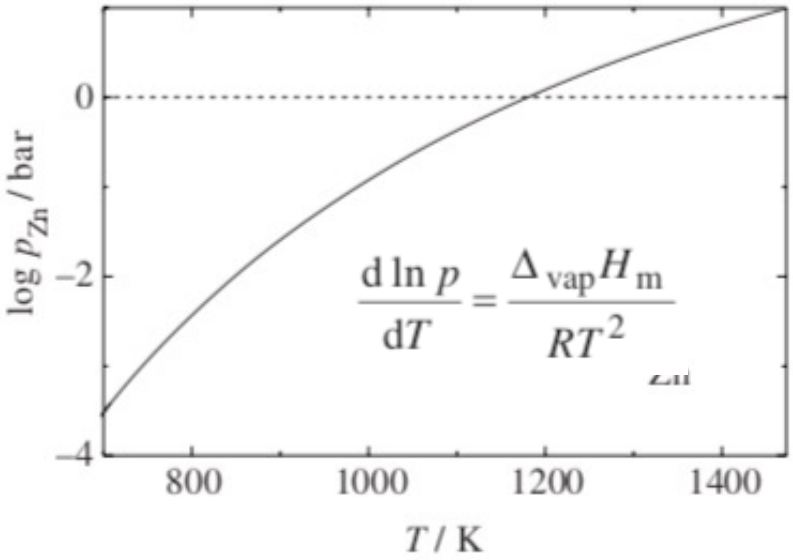


Figure 2.4 The initial dT/dp slope of selected first-order phase transitions relative to the transition temperature at p = 1 bar. Data taken from [6,7].

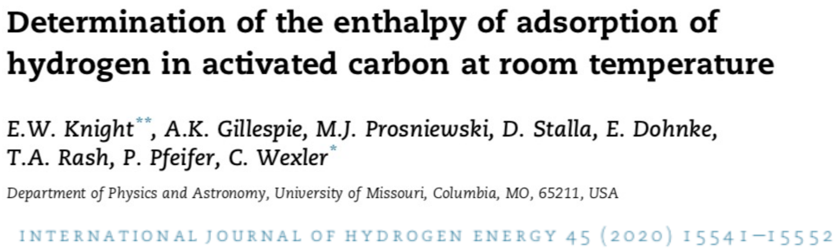
Clausius-Clapeyron Equation



$$\frac{d\ln p}{dT} = \frac{\Delta_{vap}H_m}{RT^2}$$

Figure 2.5 The vapour pressure of pure Zn as a function of temperature. The standard boiling (or vaporization) temperature is defined by the temperature at which the pressure of Zn is 1 bar.

Consider absorption of a gas on a surface
First order transition from a vapor to an absorbed layer



Determination of the enthalpy of adsorption of hydrogen in activated carbon at room temperature

E.W. Knight[**], A.K. Gillespie, M.J. Prosniewski, D. Stalla, E. Dohnke, T.A. Rash, P. Pfeifer, C. Wexler[*]

Department of Physics and Astronomy, University of Missouri, Columbia, MO, 65211, USA

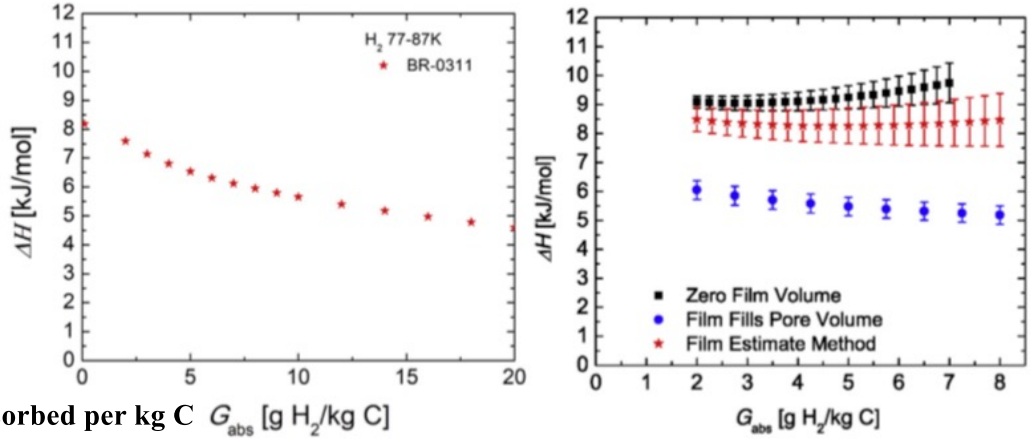
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 45 (2020) 15541–15552

Find the equilibrium pressure and temperature for a monolayer of absorbed hydrogen on a mesoporous carbon storage material

$\ln[p^{Sat}/ p_R^{Sat}] = (-\Delta H_{vap}/R) [1/T – 1/T_R]$

Use Clausius–Clapeyron Equation to determine the enthalpy of absorption

$$\Delta H = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_2}{P_1},$$



G = g H_2 Absorbed per kg C

Fig. 11 – (a) Enthalpy of adsorption calculated of BR-0311 using 77 and 87 K isotherms (Eq. (3)). (b) Enthalpy of adsorption using three different film volumes at room temperature (273 and 293 K): (i) the calculated film volumes from the Ono-Kondo fits (red), (ii) the film volume equal to zero $G_{abs} = G_{ex}$ (isoexcess) (black), and (iii) the film volume equal to the pore volume $G_{abs} = G_{st}$ (isostorage, see Appendix A) (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Van’t Hoff Equation (Looks like Clausius Clapyron Equation)

For a chemical reaction the equilibrium constant Keq = product($x_{products}$)/product($x_{reactants}$)

$\Delta G = -RT\ln K_{eq} = \Delta H - T\Delta S$

$\ln K_{eq} = -\Delta H/RT + \Delta S/R$

$d(\ln K_{eq})/dT = +\Delta H_{rxn}/RT^2$ **Van’t Hoff Equation**
(Henry’s law constant is treated as an equilibrium reaction constant)

For mixtures
Dilute: Henry’s Law Partial Pressure, $p_i = H_{ij}\,x_i$, H_{ij} **follows** $d(\ln H_{ij})/dT = \Delta H_{ij}/RT^2$
Ideal: Raoult’s Law Partial Pressure, $p_i = p_{sat}\,x_i$

$d(\ln p^{Sat})/dT = \Delta H_{vap}/(RT_{vap}^2)$ **Clausius-Clapeyron Equation**

Second Order Transition

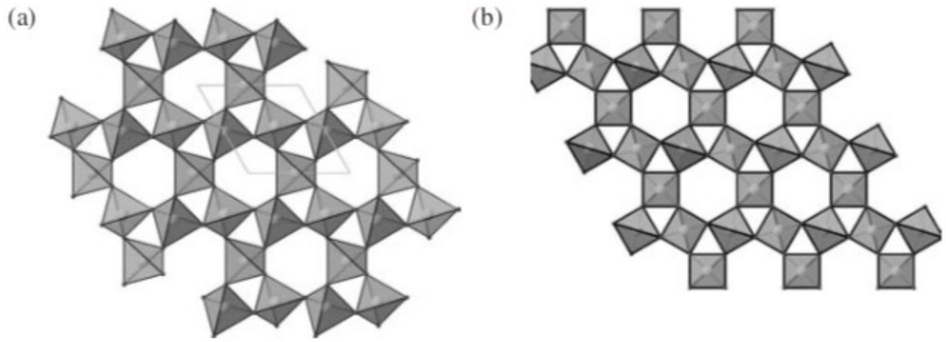


Figure 2.2 Crystal structure of α- (low) and β- (high) quartz (SiO_2).

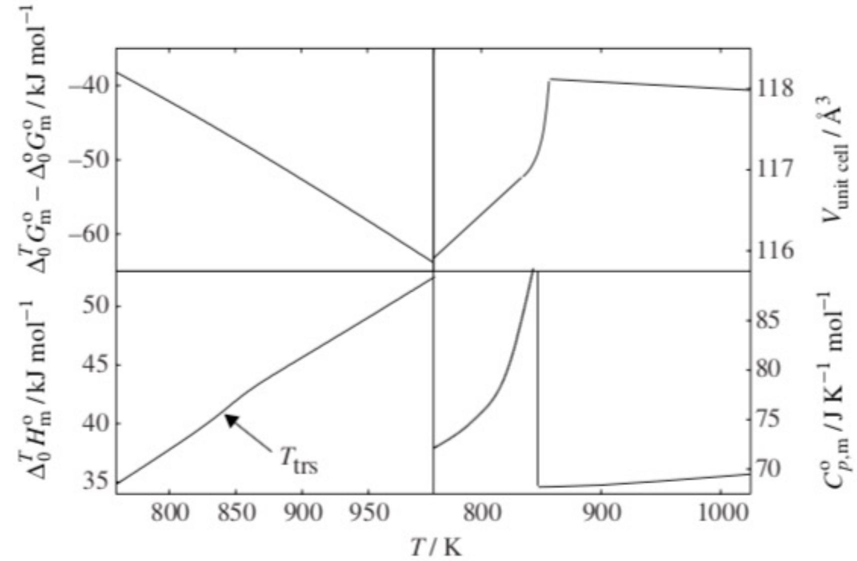


Figure 2.3 The temperature variation of the Gibbs energy [5], unit-cell volume [4] enthalpy and heat capacity [5] at the second-order α- to β-quartz transition of SiO_2. Second-order derivatives of the Gibbs energy like the heat capacity have discontinuities at the transition temperature.

$\alpha = (1/V)\,(\partial V/\partial T)_p$
$\kappa_T = (1/V)\,(\partial V/\partial P)_T$

What About a Second Order Transition?
For Example: Glass Transition T_g versus P?

There is only one “phase” present. A flowing phase and a “locked-in” phase for T_g.
There is no discontinuity in H, S, V

$$dV = 0 = (\partial V/\partial T)_p\, dT + (\partial V/\partial p)_T\, dp = V\alpha dT - V\kappa_T dp$$

$$dp/dT_g = \Delta\alpha/\Delta\kappa_T$$

T_g should be linear in pressure.

On the pressure dependence of the thermodynamical scaling exponent γ

R. Casalini *[a] and T. C. Ransom †[ab]

[a] Naval Research Laboratory, Chemistry Division, Washington, DC 20375-5342, USA. E-mail: riccardo.casalini@nrl.navy.mil

[b] American Society for Engineering Education, Washington, D.C. 20036-2479, USA

† Current address: Naval Surface Warfare Center, Indian Head Explosive Ordnance Disposal Technology Division, Indian Head, MD 20640, USA.

Soft Matter, 2020, 16, 4625

x is the dielectric relaxation time

Glass transition depends on the rate of observation, so you need to fix a rate of observation to determine the transition temperature.

liquids: *o*-terphenyl (OTP), $\gamma_S = 5.3$,[33,34] 1,1′-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC), $\gamma_S = 8.5$,[35,36] phenylphthalein-dimethylether (PDE), $\gamma_S = 4.5$,[37,38] and three polychlorinated byphenyls (PCB42, PCB54 and PCB62), found to have very different values of γ_S (PCB42 $\gamma_S = 5.5$, PCB54 $\gamma_S = 6.7$ and PCB62 $\gamma_S = 8.5$).[39] In particular, between these materials

$$dp/dT_g = \Delta\alpha/\Delta\kappa_T$$

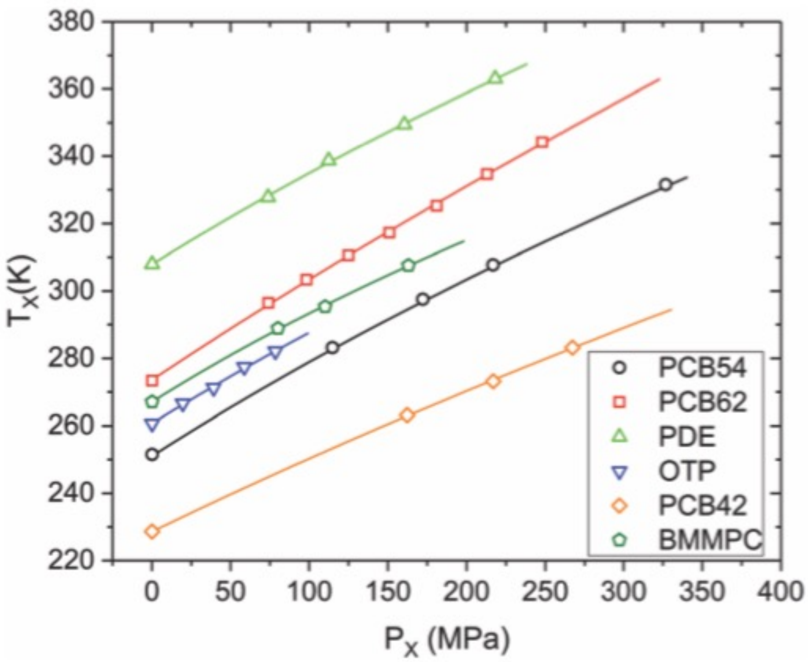
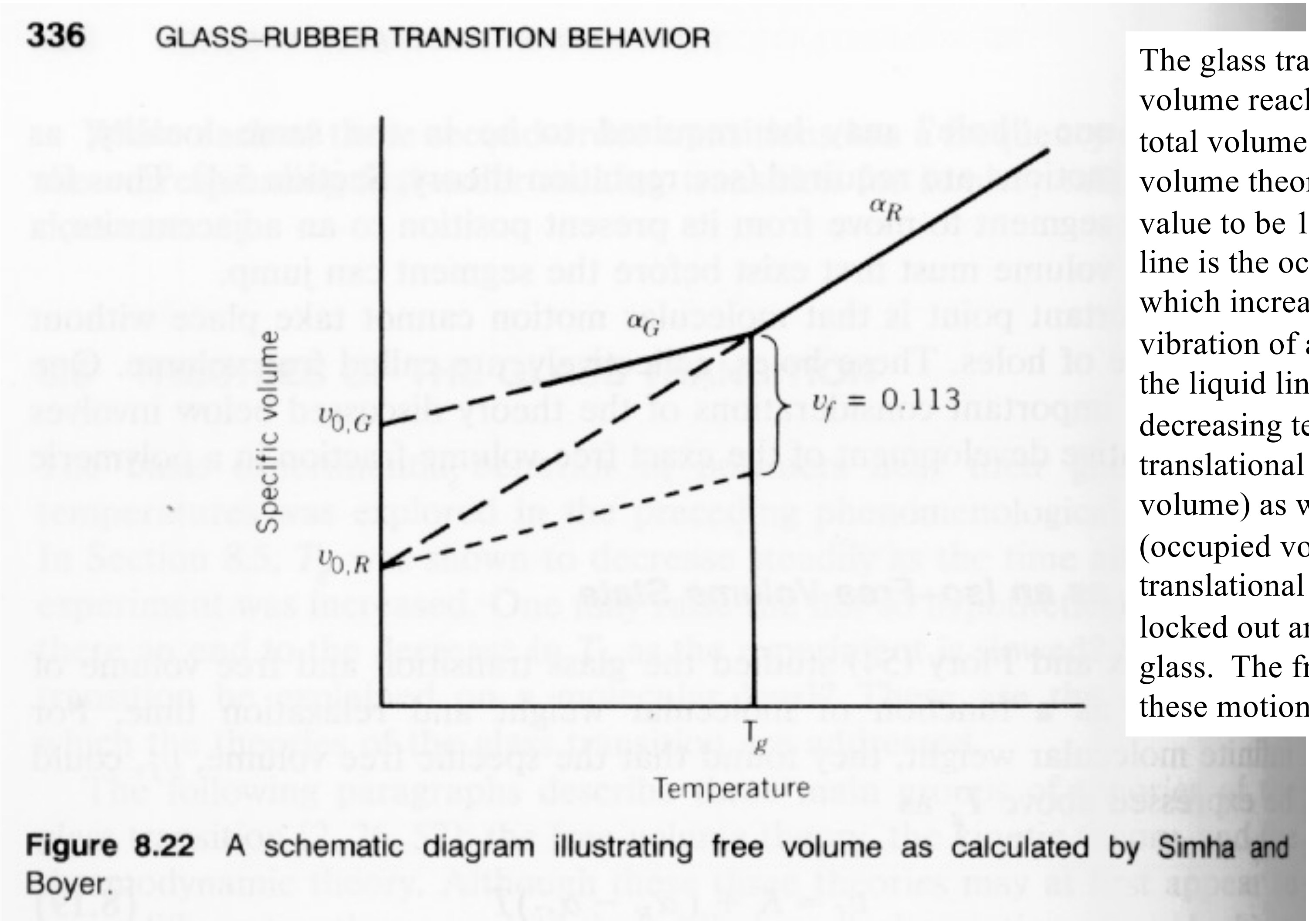


Fig. 1 Temperature T_X *versus* pressure P_X at constant relaxation time for six nonassociated liquids. The points are experimental data and the line are the best fit to the AA equation (eqn (8)). The best-fit parameters are reported in Table 1.



336 GLASS–RUBBER TRANSITION BEHAVIOR

Figure 8.22 A schematic diagram illustrating free volume as calculated by Simha and Boyer.

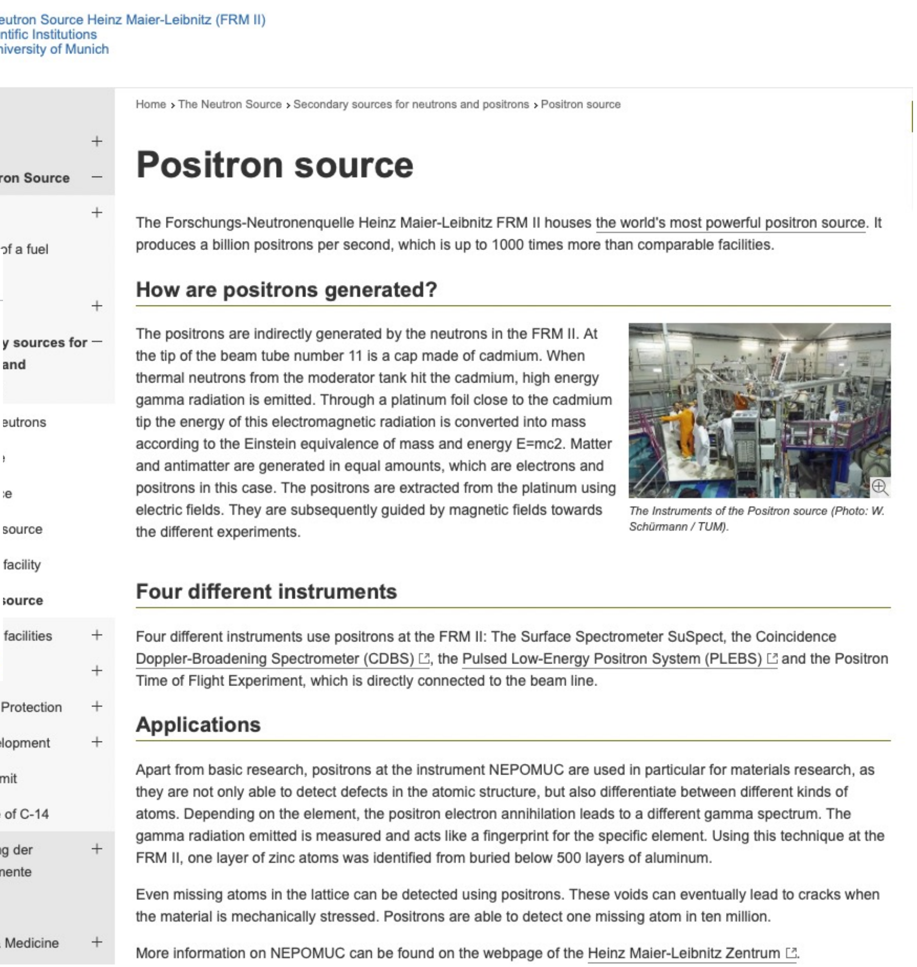
The glass transition occurs when the free volume reaches a fixed percent of the total volume according to the iso-free volume theory. This figure shows this value to be 11.3%. The bottom dashes line is the occupied volume of molecules, which increases with temperature due to vibration of atoms. The right solid line is the liquid line which decreases with decreasing temperature due to reduced translational and rotational motion (free volume) as well as molecular vibrations (occupied volume). At about 10% the translational and rotational motion is locked out and the material becomes a glass. The free volume associated with these motions is locked in at T_g.

From L. H. Sperling, "Introduction to Physical Polymer Science, 2'nd Ed."

336 GLASS–RUBBER TRANSITION BEHAVIOR

https://www.frm2.tum.de/en/frm2/secondary-sources/positron-source/

https://en.wikipedia.org/wiki/Electron–positron_annihilation


Research Neutron Source Heinz Maier-Leibnitz (FRM II)
Central Scientific Institutions
Technical University of Munich

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- Discharge of C-14
- Entsorgung der Brennelemente +
- Research
- Industry & Medicine +

Home › The Neutron Source › Secondary sources for neutrons and positrons › Positron source

Positron source

The Forschungs-Neutronenquelle Heinz Maier-Leibnitz FRM II houses the world's most powerful positron source. It produces a billion positrons per second, which is up to 1000 times more than comparable facilities.

How are positrons generated?

The positrons are indirectly generated by the neutrons in the FRM II. At the tip of the beam tube number 11 is a cap made of cadmium. When thermal neutrons from the moderator tank hit the cadmium, high energy gamma radiation is emitted. Through a platinum foil close to the cadmium tip the energy of this electromagnetic radiation is converted into mass according to the Einstein equivalence of mass and energy E=mc2. Matter and antimatter are generated in equal amounts, which are electrons and positrons in this case. The positrons are extracted from the platinum using electric fields. They are subsequently guided by magnetic fields towards the different experiments.

The Instruments of the Positron source (Photo: W. Schürmann / TUM).

Four different instruments

Four different instruments use positrons at the FRM II: The Surface Spectrometer SuSpect, the Coincidence Doppler-Broadening Spectrometer (CDBS), the Pulsed Low-Energy Positron System (PLEBS) and the Positron Time of Flight Experiment, which is directly connected to the beam line.

Applications

Apart from basic research, positrons at the instrument NEPOMUC are used in particular for materials research, as they are not only able to detect defects in the atomic structure, but also differentiate between different kinds of atoms. Depending on the element, the positron electron annihilation leads to a different gamma spectrum. The gamma radiation emitted is measured and acts like a fingerprint for the specific element. Using this technique at the FRM II, one layer of zinc atoms was identified from buried below 500 layers of aluminum.

Even missing atoms in the lattice can be detected using positrons. These voids can eventually lead to cracks when the material is mechanically stressed. Positrons are able to detect one missing atom in ten million.

More information on NEPOMUC can be found on the webpage of the Heinz Maier-Leibnitz Zentrum.


Electron–positron annihilation

From Wikipedia, the free encyclopedia

Electron–positron annihilation occurs when an electron (e^-) and a positron (e^+, the electron's antiparticle) collide. At low energies, the result of the collision is the annihilation of the electron and positron, and the creation of energetic photons:

$$e^- + e^+ \rightarrow \gamma + \gamma$$

At high energies, other particles, such as B mesons or the W and Z bosons, can be created. All processes must satisfy a number of conservation laws, including:

- Conservation of electric charge. The net charge before and after is zero.
- Conservation of linear momentum and total energy. This forbids the creation of a single photon. However, in quantum field theory this process is allowed; see examples of annihilation.
- Conservation of angular momentum.
- Conservation of total (i.e. net) lepton number, which is the number of leptons (such as the electron) minus the number of antileptons (such as the positron); this can be described as a conservation of (net) matter law.

As with any two charged objects, electrons and positrons may also interact with each other without annihilating, in general by elastic scattering.

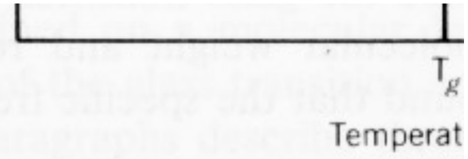


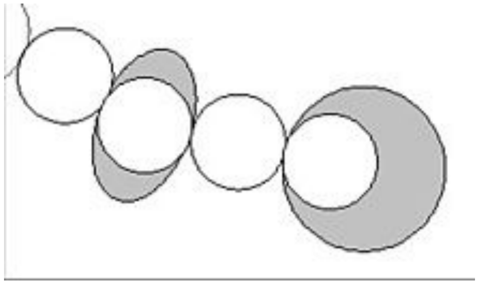
Figure 8.22 A schematic diagram illustrating free
Boyer.

From L. H. Sperling, "Introduction to Physical Polymer Science, 2'nd Ed."

Number of end-groups = $2/M_n$

Flory-Fox Equation

$$T_g = T_{g,\infty} - \frac{K}{M_n}$$



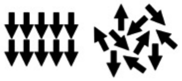
End groups have more free volume
T_g occurs when the free volume
reaches less than $V_{free} \leq 0.113V$

Fox Equation

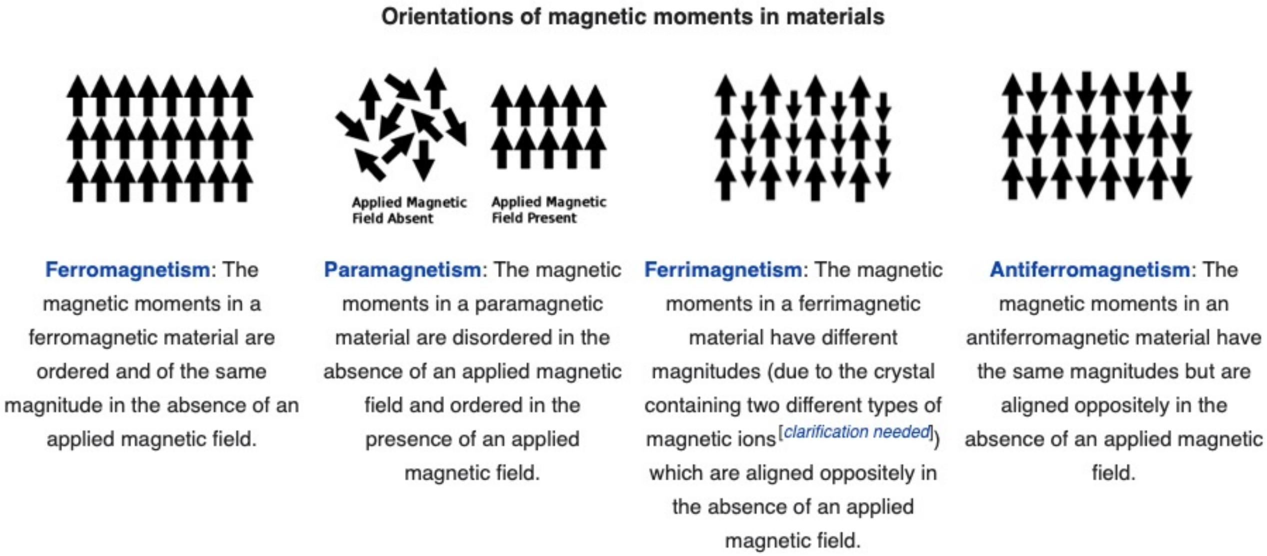
$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

This indicates that the parameter of interest is $1/T_g$
T_g is the temperature where a certain free volume is found due to thermal expansion, $V = V_{occupied} + V_{free} = V_0 + V\alpha_T dT$
T_g is the temperature where $V_{free}/V = 0.113$

Some other second order transitions:



Curie Temperature (permanent magnetism disappears Ferro to Para magnetic)
Neel Temperature (antiferromagnetic becomes paramagnetic)
Ferro to Para Magnetic (Curie Temp)
Ferri to Para Magnetic (Neel Temp)



Orientations of magnetic moments in materials

Ferromagnetism: The magnetic moments in a ferromagnetic material are ordered and of the same magnitude in the absence of an applied magnetic field.

Paramagnetism: The magnetic moments in a paramagnetic material are disordered in the absence of an applied magnetic field and ordered in the presence of an applied magnetic field.

Ferrimagnetism: The magnetic moments in a ferrimagnetic material have different magnitudes (due to the crystal containing two different types of magnetic ions[*clarification needed*]) which are aligned oppositely in the absence of an applied magnetic field.

Antiferromagnetism: The magnetic moments in an antiferromagnetic material have the same magnitudes but are aligned oppositely in the absence of an applied magnetic field.

Usually Second order transition Neel Temperature (like Curie Temp for antiferromagnetic) $Fe_{0.947}O$
Some cases First order transition (shown here for $Fe_{0.99}O$)

$(\partial H/\partial T)_p = C_p$

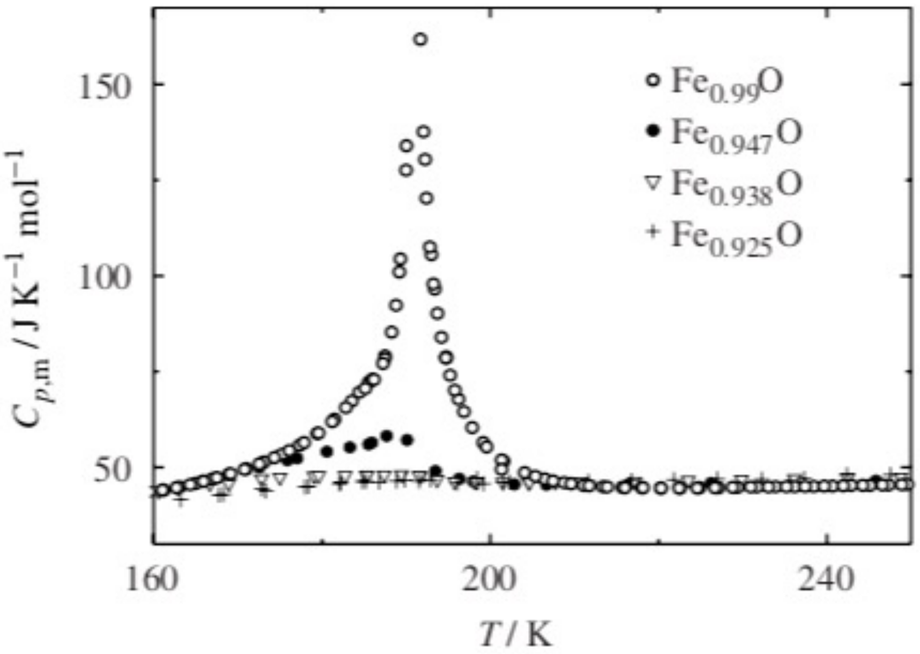


Figure 2.13 Heat capacity of wüstite around the Néel temperature [19]. ○: $Fe_{0.99}O$; ●: $Fe_{0.947}O$; ∇: $Fe_{0.938}O$; +: $Fe_{0.925}O$. Reproduced by permission of the Mineralogical Society of America.

[19] S. Stølen, R. Glöckner, F. Grønvold, T. Atake and S. Izumisawa, *Am. Mineral.* 1996, **81**, 973.

Inden Model $\tau = T/T_{tr}$

For $\tau < 1$

$$C_p^{\mathrm{mag}} = K^{\mathrm{L}} R \frac{\ln(1+\tau^3)}{\ln(1-\tau^3)}$$

For $\tau > 1$

$$C_p^{\mathrm{mag}} = K^{\mathrm{S}} R \frac{\ln(1+\tau^5)}{\ln(1-\tau^5)}$$

First-order antiferromagnetic transitions of $SrMn_2P_2$ and $CaMn_2P_2$ single crystals containing corrugated-honeycomb Mn sublattices

PNAS 2021 Vol. 118 No. 44 e2108724118

N. S. Sangeetha[a,1], Santanu Pakhira[a], Qing-Ping Ding[a,b], Lennard Krause[c,d], Hyung-Cheol Lee[a,b], Volodymyr Smetana[e], Anja-Verena Mudring[c,d,e], Bo Brummerstedt Iversen[c,d], Yuji Furukawa[a,b], and David C. Johnston[a,b,2]

[a]Ames Laboratory, Iowa State University, Ames, IA 50011; [b]Department of Physics and Astronomy, Iowa State University, Ames, IA 50011; [c]Center for Materials Crystallography, Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark; [d]iNANO, Aarhus University, DK-8000 Aarhus C, Denmark; and [e]Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden

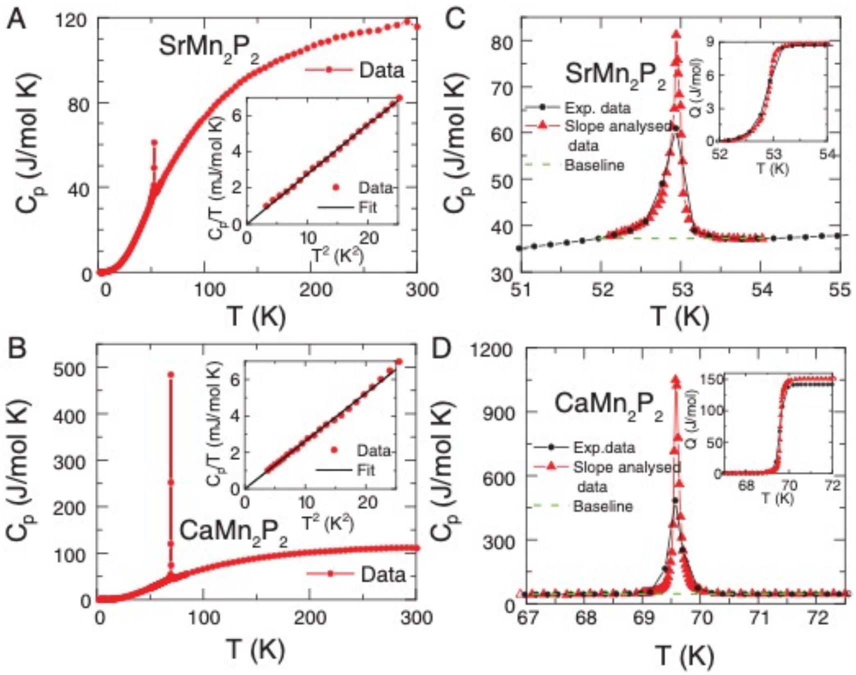


Fig. 5. Heat capacity C_p versus temperature T for (*A*) $SrMn_2P_2$ and (*B*) $CaMn_2P_2$ single crystals. (*A* and *B*, *Insets*) $C_p(T)/T$ versus T^2 for $T \leq 5$ K, where the straight lines through the respective data are fits by Eq. **1**. A comparison of the conventionally measured $C_p(T)$ and single-pulse slope-analyzed $C_p(T)$ (using a heating curve) is shown for (*C*) $SrMn_2P_2$ and (*D*) $CaMn_2P_2$ crystals. (*C* and *D*, *Insets*) The latent heat associated with the first-order magnetic transition (FOMT). The $C_p(T)$ values at the FOMT are estimated by subtracting the polynomial-fitted baseline data (dashed green line) from the total $C_p(T)$ data in that temperature region shown in *C* and *D*.

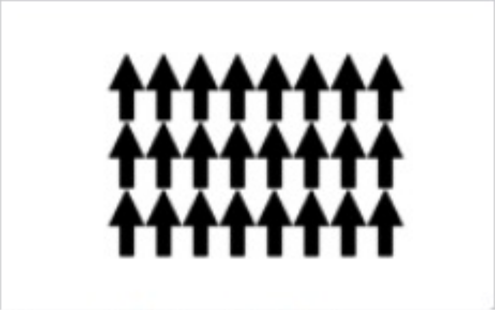


Figure 1. Below the Curie temperature, neighbouring magnetic spins align parallel to each other in ferromagnet in the absence of an applied magnetic field

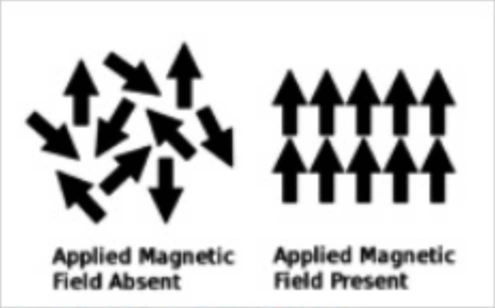


Figure 2. Above the Curie temperature, the magnetic spins are randomly aligned in a paramagnet unless a magnetic field is applied

Landau theory for 2'nd order transitions based on a Taylor series expansion of the Gibbs free energy in the "Order Parameter" Γ

-The free energy is analytic (there is a function)
-The free energy is symmetric in T (only even powers of T)

The order parameter was originally the magnetization, m
For liquid crystals it is the director
For binary blends it can be the composition

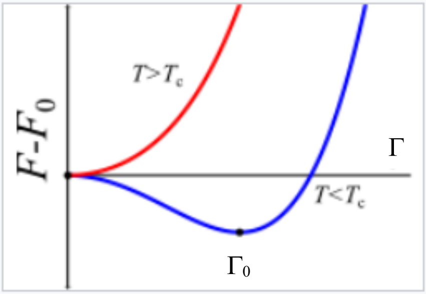
Curie Temperature is the critical point for ordering. Above T_c no order and m = 0 in the absence of a magnetic field, i.e. paramagnetism

Below T_c, m has a value.

$$\Delta_{\text{trs}} G = \Delta_{\text{trs}} G(T, p, \Gamma)$$

At constant T and p

$$\Delta_{\text{trs}} G = a\Gamma + \frac{1}{2} b\Gamma^2 + \frac{1}{3} c\Gamma^3 + \frac{1}{4} d\Gamma^4 + \dots$$

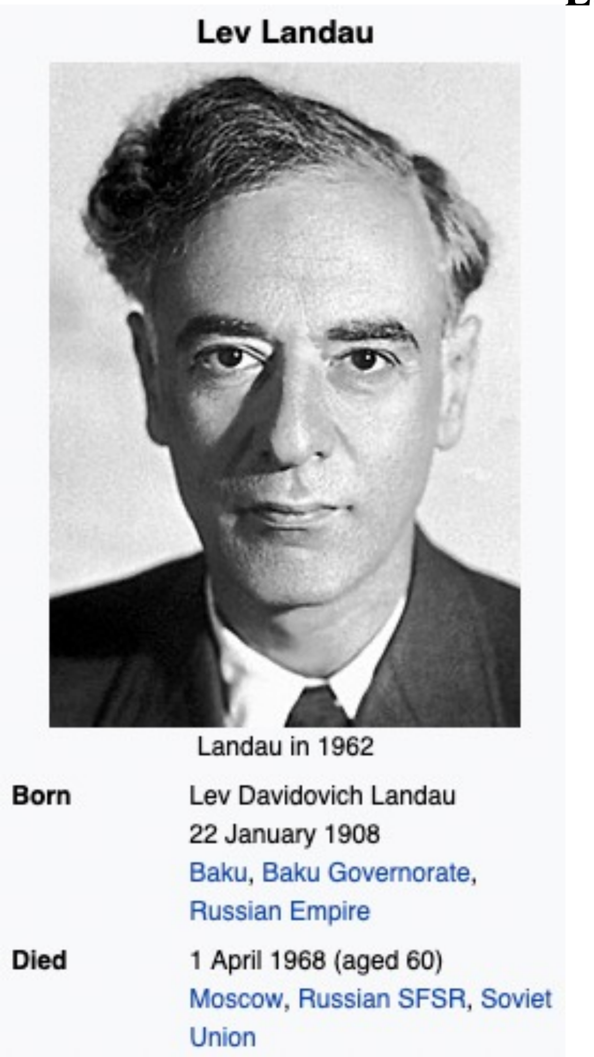


Sketch of free energy as a function of order parameter Γ

"a" is a bias associated with the direction of magnetization, this is 0 above T_c
"b" is positive above T_c and changes sign at T_c

$$b = B(T - T_{\text{trs}})$$

Landau theory for order parameter



Lev Landau

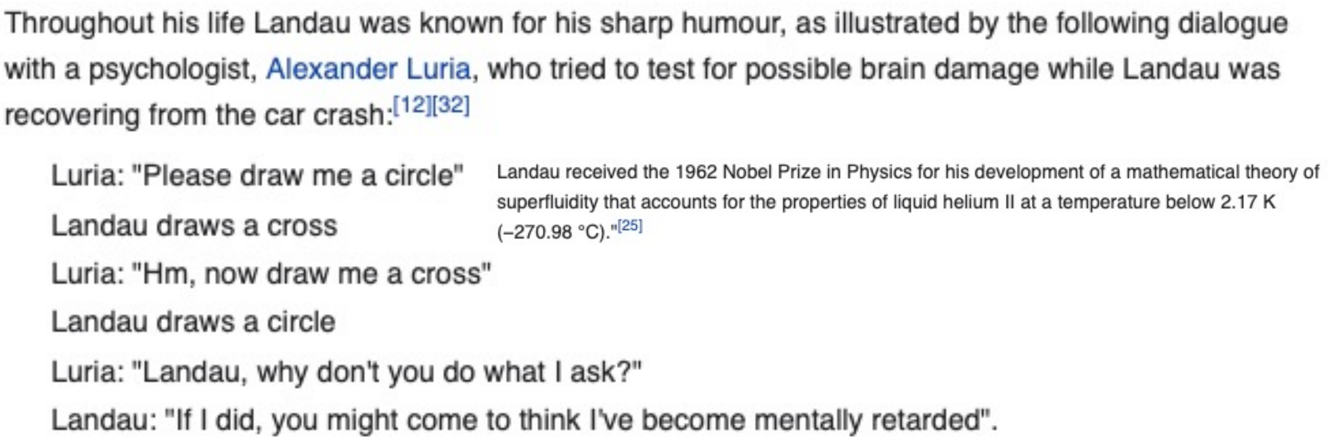
Landau in 1962

Born	Lev Davidovich Landau 22 January 1908 Baku, Baku Governorate, Russian Empire
Died	1 April 1968 (aged 60) Moscow, Russian SFSR, Soviet Union

On 27 April 1938, Landau was arrested for a leaflet which compared Stalinism to German Nazism and Italian Fascism.[17][23] He was held in the NKVD's Lubyanka prison until his release, on 29 April 1939, after Pyotr Kapitsa, an experimental low-temperature physicist and the founder and head of the institute, wrote a letter to Joseph Stalin in which he personally vouched for Landau's behaviour and

Photo in prison, 1938-9

Landau led a team of mathematicians supporting Soviet atomic and hydrogen bomb development. He calculated the dynamics of the first Soviet thermonuclear bomb, including predicting the yield. For this work Landau received the Stalin Prize in 1949 and 1953, and was awarded the title "Hero of Socialist Labour" in 1954.[17]



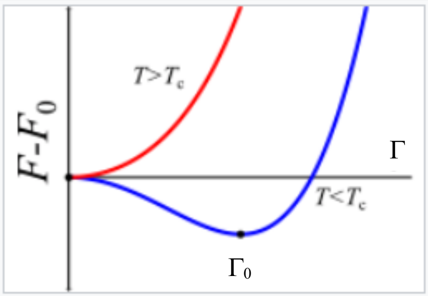
Throughout his life Landau was known for his sharp humour, as illustrated by the following dialogue with a psychologist, Alexander Luria, who tried to test for possible brain damage while Landau was recovering from the car crash:[12][32]

> Luria: "Please draw me a circle"
> Landau draws a cross
> Luria: "Hm, now draw me a cross"
> Landau draws a circle
> Luria: "Landau, why don't you do what I ask?"
> Landau: "If I did, you might come to think I've become mentally retarded".

Landau received the 1962 Nobel Prize in Physics for his development of a mathematical theory of superfluidity that accounts for the properties of liquid helium II at a temperature below 2.17 K (−270.98 °C)."[25]

Landau theory for 2'nd order transitions

The **order parameter** $\boldsymbol{\Gamma}$ could be concentration (normal phase separation), magnetization (magnets) , orientation (LCs)
The point is to find a value for $\boldsymbol{\Gamma}$ above and below the critical point T_c (where phase separation become possible).
Particularly above T_c, $\boldsymbol{\Gamma} = 0$ and we have no "order" (think of no magnetization above the Curie temperature or no deviation from the average composition ($\rho - < \rho >$) above the critical temperature).



Sketch of free energy as a function of order parameter Γ

-The free energy is analytic (there is a function in Γ and T)
-The free energy F is symmetric in Γ (only even powers of Γ)

For simplicity, take a two term Taylor series expansion $\Delta F = a(T)\, \Gamma^2 + b(T)/2\, \Gamma^4$
Near the critical temperature assume for simplicity

$$\Delta F = a_0\,(T - T_c)\, \Gamma^2 + b_0/2\, \Gamma^4$$

For a solution to Γ, you must have $b_0 > 0$ (this is obvious below); and $a(T)$ must change sign for phase separation to occur at T_c so $a(T) = a_0\,(T - T_c)$

At the critical point $\partial F/\partial \Gamma = 0 = 2a_0\,(T - T_c)\, \Gamma_0 + 2b_0\, \Gamma_0^3$
To minimize free energy and make a stable phase either $\Gamma_0 = 0$ (above T_c) or $\Gamma_0^2 = -\, a_0\,(T - T_c)/b_0$ (for $T \leq T_c$)
For $T \leq T_c$, $\Gamma_0 \sim (T - T_c)^{1/2}$ The critical exponent is ½ for Landau theory.

Landau theory for 2’nd order transitions

-S U V
H A
-p G T

$dH = VdP + TdS$

$C_p = (\partial H/\partial T)_P = T\,(\partial S/\partial T)_P$

$G = \Delta F = H - TS$

$(d\Delta F/dT) = (dH/dT) - T(dS/dT) - S$

$(d^2\Delta F/dT^2) = -(dS/dT) = -C_p/\mathrm{T}$

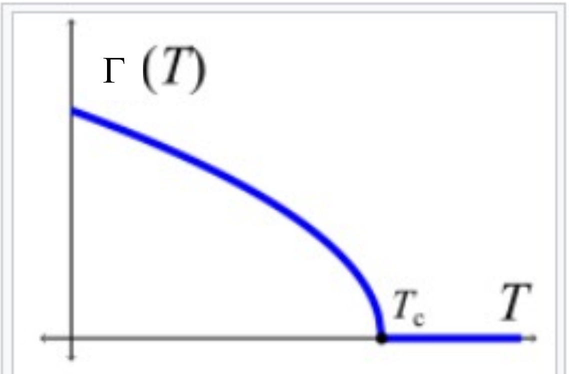
$C_p = -\mathrm{T}\,(d^2\Delta F/dT^2)$

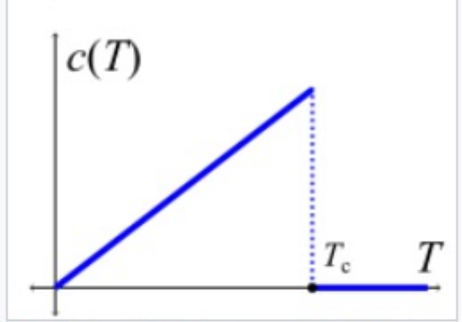
$\Delta F = a_0\,(T - T_c)\,\Gamma^2 + b_0/2\ \Gamma^4$

$\Gamma_0 = 0$ (above T_c) and $\Gamma_0^2 = -\,a_0\,(T - T_c)/b_0$ (for $T \le T_c$)

$\Delta F = 0$ (above T_c) and $\Delta F = -a_0^2\,(T - T_c)^2/b_0 + a_0^4/2\,(T - T_c)^2/b_0 = -a_0^2\,(T - T_c)^2/2b_0$

$C_p = 0$ (above T_c) ; and $C_p = -\mathrm{T}\,(d^2\Delta F/dT^2) = \mathrm{T}\,a_0^2/b_0$ (for $T \le T_c$)





Order parameter and specific heat as a function of temperature

Discontinuity in the second derivative of free energy (C_p) at the transition temperature **indicates a second order transition**.

For a first order transition the jump at the transition temperature in C_P would have been infinite, not $\Delta C_P = T_c\,a_0^2/b_0$ and Γ would not be continuous.

One of two Landau approaches for 1'st order transitions

This approach looks very similar to the virial equation of state of Onnes

$\Delta F = A(T)\,\Gamma^2 - B_0\,\Gamma^4 + C_0\,\Gamma^6$

First term negative above T_0, second term negative, third term positive

$A(T) = A_0\,(T - T_0)$; T_0 is a temperature where A(T) changes sign (not T_c)

A_0, B_0, C_0 are positive and constant

i) $T > T^*$ (and $T > T_0$), $\Delta F(\Gamma)$ increases for all Γ so minimum is at $\Gamma_0 = 0$

ii) $T < T^*$, $\Delta F(\Gamma)$ decreases in Γ from Γ=0 to a minimum at $\pm\,\Gamma_0(T)$ with $\Delta F < 0$

iii) $T_0 < T < T^*$, $\Delta F(T)$ decreases then discontinuously drops to 0 at T^*

To find T^*

1) $\Delta F = 0$

$0 = A(T)\,\Gamma^2 - B_0\,\Gamma^4 + C_0\,\Gamma^6$ so, $A(T) = B_0\,\Gamma^2 - C_0\,\Gamma^4$

2) $d\Delta F/d\Gamma = 0$

$0 = 2A(T)\,\Gamma - 4B_0\,\Gamma^3 + 6C_0\,\Gamma^5$ so, $A(T) = 2B_0\,\Gamma^2 - 3C_0\,\Gamma^4$

or, $B_0 - C_0\,\Gamma^2 = 2B_0 - 3C_0\,\Gamma^2$

$\Gamma^2(T^*) = B_0/2C_0$

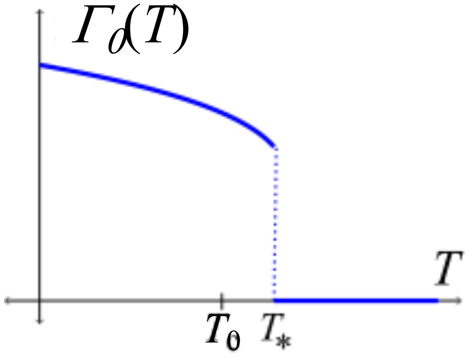
3) From 1) $A(T) = B_0\,\Gamma^2 - C_0\,\Gamma^4$

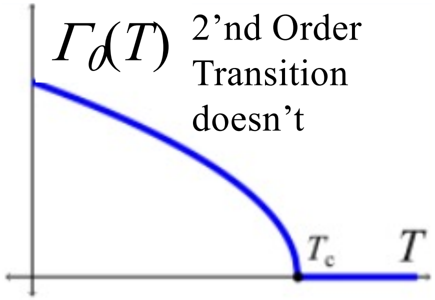
And $A(T^*) = B_0\,(B_0/2C_0) - C_0\,(B_0/2C_0)^2 = B_0^2/4C_0$

$A(T^*) = A_0\,(T^* - T_0)$ so, $T^* = T_0 + B_0^2/(4\,A_0\,C_0)$

Landau invented the terms first and second order transition from this model.

1'st Order Transition shows a discontinuity in Γ_0(T)





2'nd Order Transition doesn't

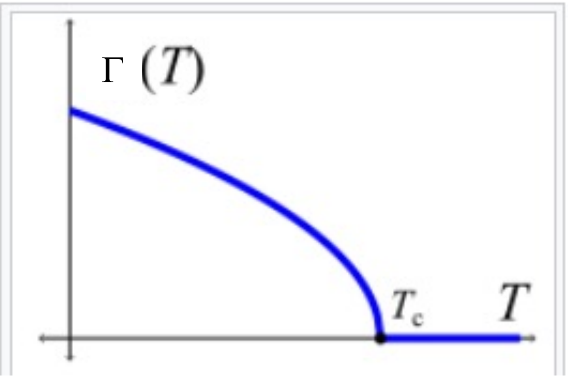
At the Curie transition (second order transition)

$$\frac{\partial \Delta_{\text{trs}} G}{\partial \Gamma} = 0 \quad \text{and} \quad \frac{\partial^2 \Delta_{\text{trs}} G}{\partial \Gamma^2} > 0$$

$$\Delta_{\text{trs}} G = \frac{1}{2} b\Gamma^2 + \frac{1}{3} c\Gamma^3 + \frac{1}{4} d\Gamma^4 + \ldots$$

$$\frac{\partial \Delta_{\text{trs}} G}{\partial \Gamma} = B(T - T_{\text{trs}})\Gamma + d\Gamma^3 = 0$$

$$\Gamma^2 = -\frac{B}{d}(T - T_{\text{trs}}) \quad \text{for} \quad T < T_{\text{trs}}$$



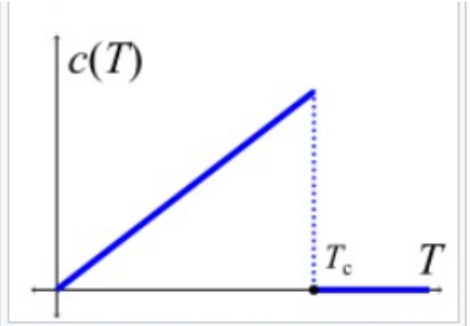
Order parameter is 1 at 0 K so $\frac{B}{d} = \frac{1}{T_{\text{trs}}}$ and $\Gamma = \left[\frac{T_{\text{trs}} - T}{T_{\text{trs}}}\right]^{1/2}$

The transitional Gibbs energy is for $T \leq T_{\text{trs}}$

$$\Delta_{\text{trs}} G = -\frac{B^2}{2d}(T - T_{\text{trs}})^2 + \frac{B^2}{4d}(T - T_{\text{trs}})^2 = -\frac{B^2}{4d}(T - T_{\text{trs}})^2$$

$$\Delta_{\text{trs}} S = \frac{B^2}{2d}(T - T_{\text{trs}}) = -\frac{1}{2} B \cdot \Gamma^2$$

$$C_p^{\text{trs}} = \frac{B^2}{2d} T$$



Order parameter and specific heat as a function of temperature

Single Component Phase Diagrams

For a single component, an equation of state relates the variables of the system, PVT
PV = RT or Z = 1 **Ideal Gas at low p or high T or low ρ**

$$Z \equiv \frac{P}{RT\rho} = A + B\rho + C\rho^2 + \cdots$$

Virial Equation of State

So, a phase diagram for a single component will involve two free variables, such as P vs T or T versus ρ.

Other unusual variables might also be involved such as magnetic field, electric field.
Then a 2D phase diagram would require specification of the fixed free variables.

Z is the Compressibility Factor

B is the second order virial coefficient which reflects binary interactions, ρ^2
B has units of volume and is related to the excluded volume (will see later with VDW EOS)

Single Component Phase Diagrams

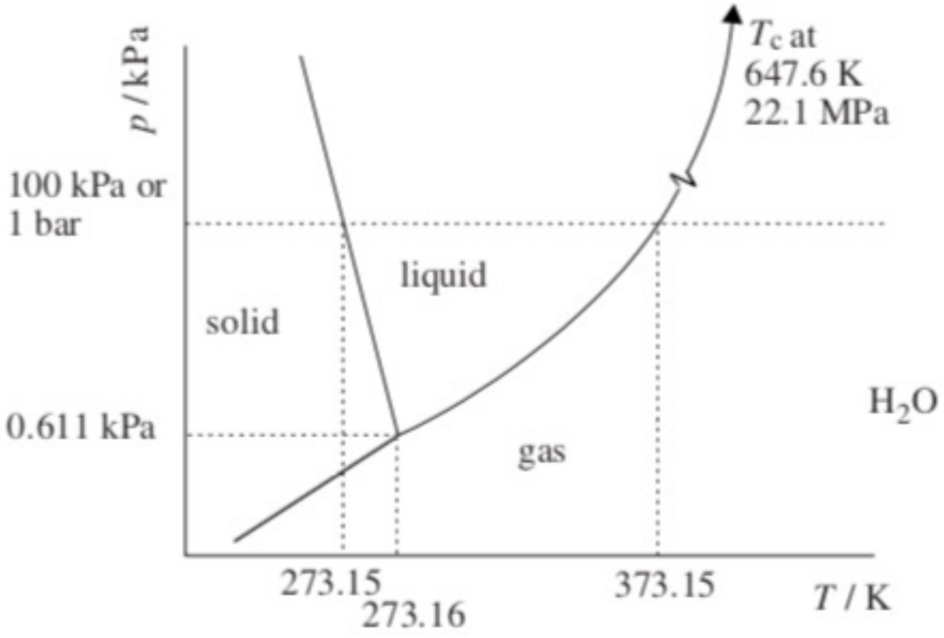


Figure 2.7 The p,T phase diagram of H_2O (the diagram is not drawn to scale).

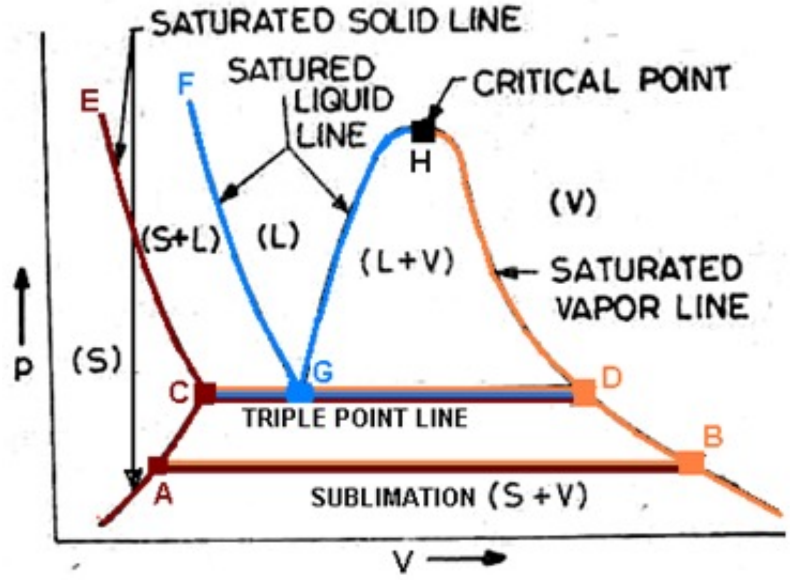
Isochoric phase diagram

Fill a piston with the material at p and T, and observe the pressure as the temperature is varied holding the volume constant

For a single component, an equation of state relates the variables of the system, PVT

$$F + Ph = C + 2 + n$$

Isothermal



Isochoric

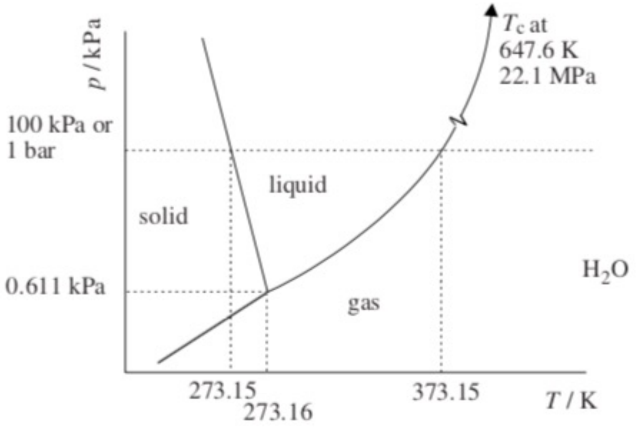
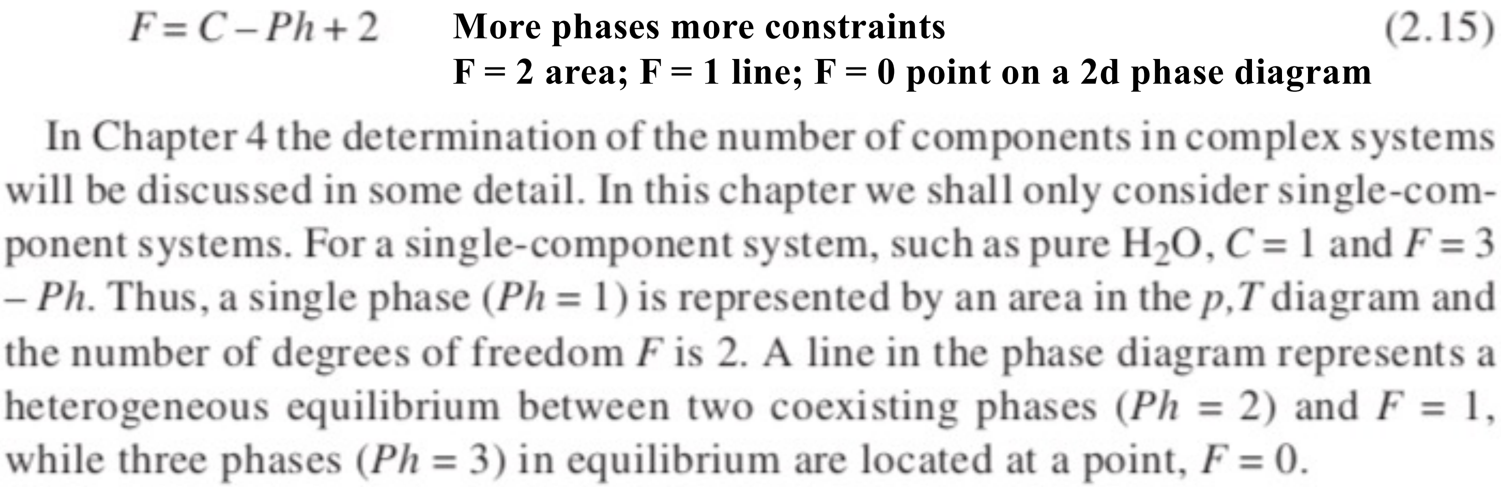


Figure 2.7 The p,T phase diagram of H_2O (the diagram is not drawn to scale).

http://ecoursesonline.iasri.res.in/mod/page/view.php?id=2406

Gibbs Phase Rule

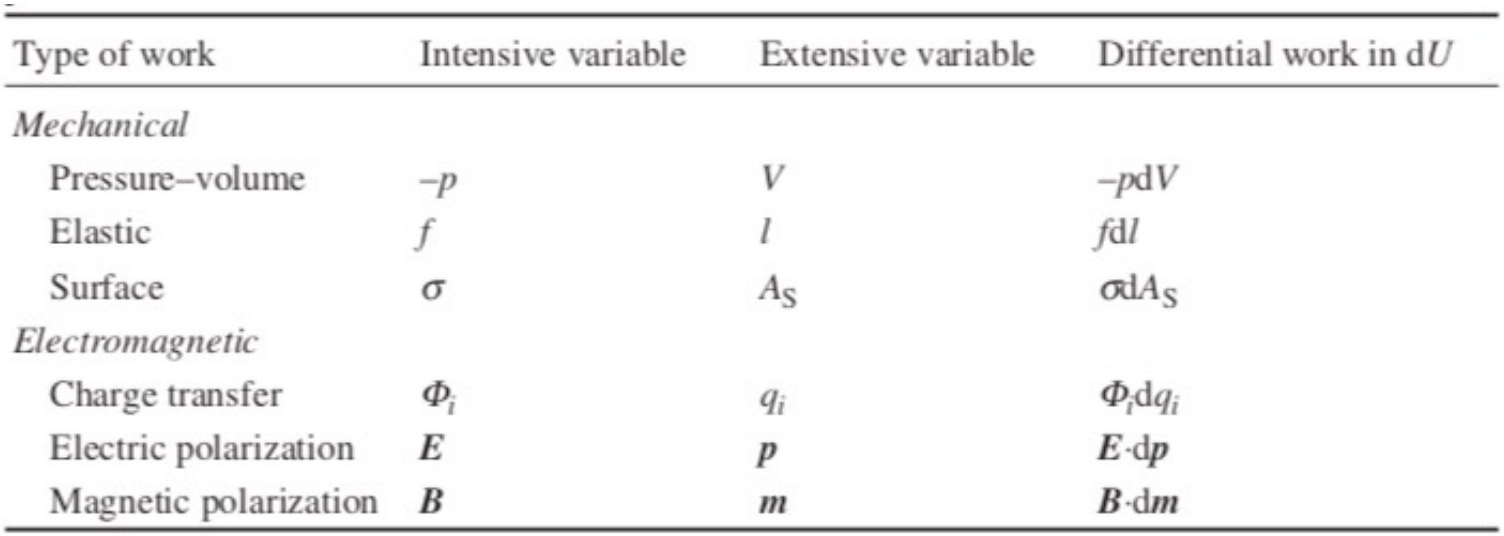
Number of DOF = Components – Phases + 2
More components more freedom
More phases more constraints
F = 2 area; F = 1 line; F = 0 point on a 2d phase diagram



$$F = C - Ph + 2 \qquad (2.15)$$

In Chapter 4 the determination of the number of components in complex systems will be discussed in some detail. In this chapter we shall only consider single-component systems. For a single-component system, such as pure H_2O, $C = 1$ and $F = 3 - Ph$. Thus, a single phase ($Ph = 1$) is represented by an area in the p,T diagram and the number of degrees of freedom F is 2. A line in the phase diagram represents a heterogeneous equilibrium between two coexisting phases ($Ph = 2$) and $F = 1$, while three phases ($Ph = 3$) in equilibrium are located at a point, $F = 0$.

Field Induced Transitions



Type of work	Intensive variable	Extensive variable	Differential work in dU
Mechanical			
Pressure–volume	$-p$	V	$-p\mathrm{d}V$
Elastic	f	l	$f\mathrm{d}l$
Surface	σ	A_S	$\sigma\mathrm{d}A_\mathrm{S}$
Electromagnetic			
Charge transfer	Φ_i	q_i	$\Phi_i\mathrm{d}q_i$
Electric polarization	$\boldsymbol{E}$	$\boldsymbol{p}$	$\boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p}$
Magnetic polarization	$\boldsymbol{B}$	$\boldsymbol{m}$	$\boldsymbol{B}\cdot\mathrm{d}\boldsymbol{m}$

Consider constant volume (isochoric) and subject to a magnetic field

-S U V
H A
-p G T

$dU = -pdV + TdS + Bdm = TdS + Bdm$
$dA = -SdT - pdV + Bdm = -SdT + Bdm$

Assume constant volume, V

Magnetic Field Strength B (intrinsic)
Magnetic Moment, m (extrinsic)
(strength of a magnet)
Magnetic moment drops with T
Torque = **m** x **B**

Legendre Transformation (isochoric dV = 0)

$dA = -SdT + Bdm$
So, A is naturally broken into functions of T and m
$(dA/dT)_m = -S$
$(dA/dm)_T = B$
$dA = (dA/dT)_m\, dT + (dA/dm)_T\, dm$

Take the second derivative
$d^2A/(dTdm) = ((d/dT)(dA/dm)_T)_m = ((d/dm)(dA/dT)_m)_T = d^2A/(dmdT)$
Using the above expressions and the middle two terms
$(dB/dT)_{m,V} = -(dS/dm)_{T,V}$
This is a Maxwell Relationship, and the process is called a Legendre transformation

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

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

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

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

Consider constant volume (isochoric) and subject to a magnetic field

-S U V
 H A
-p G T

dU = -pdV + TdS + Bdm = TdS + Bdm
dA = -SdT – pdV +Bdm = -SdT + Bdm

Assume constant volume, V

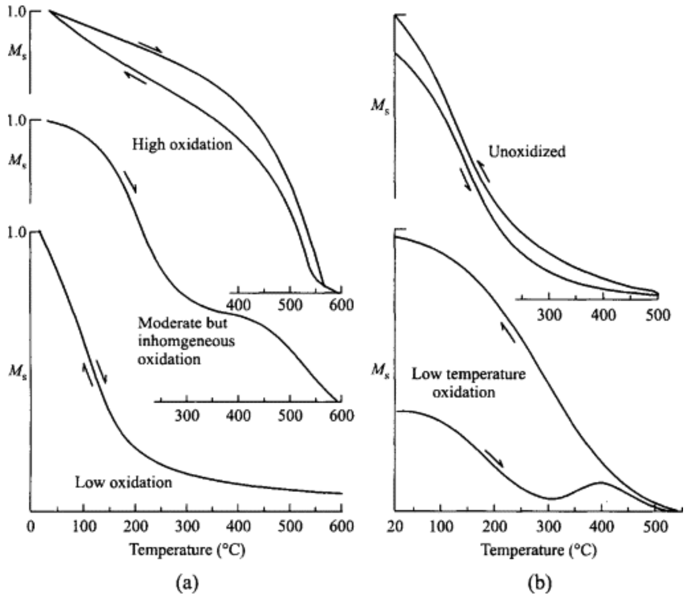
Magnetic Field Strength B
Magnetic Moment, m
(strength of a magnet)
Magnetic moment drops with T
Torque = **m** x **B**

Legendre Transformation

We want to know how the magnetic moment, m, changes with temperature at constant volume and field strength, B, $(dm/dT)_{B,V}$. *Intuitively, we know that this decreases.*

Define a Helmholtz free energy (HFE) minus the magnetic field energy, A’,
A’ = A – Bm and set its derivative to 0. This is the complete HFE for a magnetic field, (see the **Alberty paper section 4**, probably need to read the whole paper or just believe it)
dA’ = 0 = dA – Bdm – mdB = -SdT + Bdm –Bdm –mdB = -SdT –mdB = 0
We can perform a Legendre Transform on this equation yielding:
$(dm/dT)_{B,V} = (dS/dB)_{T,V}$
So, the change in magnetic moment with temperature (which decreases) is equal to the reduction in entropy with magnetic field (as the material orders).
With this extension the four Maxwell relations expand to 27 with the normal parameters and a very large number if you include the different fields in slide 16

Magnetic field strength decreases with temperature



The Curie temperature is where magnets lose their permanent magnetic field

$$(dm/dT)_{B,V} = (dS/dB)_{T,V}$$

The rate of change of magnetic moment in temperature at constant field reflects the isothermal change in entropy with magnetic field. At the Curie Temperature entropy doesn’t change with field at constant temperature.

Ising Model

Gibbs Phase Rule with n additional components

$$F + Ph = C + 2 + n$$

Degrees of freedom, F plus number of phases Ph, equals the number of components, C ,plus 2 plus the number of additional components considered, n.

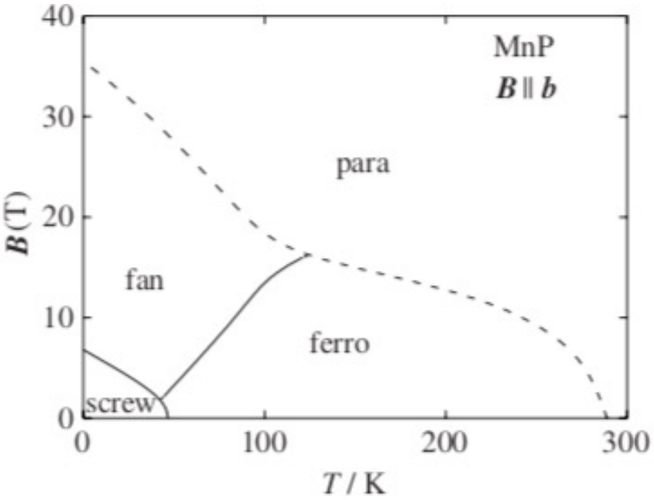


Figure 2.9 The B–T phase diagram of MnP [13] with the magnetic field along the b-axis. Three different magnetically ordered phases – ferro, fan and screw – are separated by first-order phase transitions. The transitions to the disordered paramagnetic state are of second order and given by a dashed line.

Equations of State for Gasses

Ideal Gas: pV = RT p = ρRt Z = 1

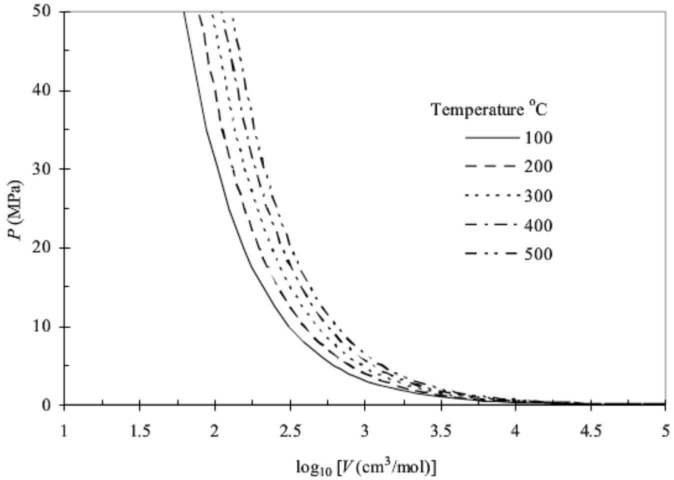


Figure 1.3 *Ideal gas behavior at five temperatures.*

P ~ 1/V

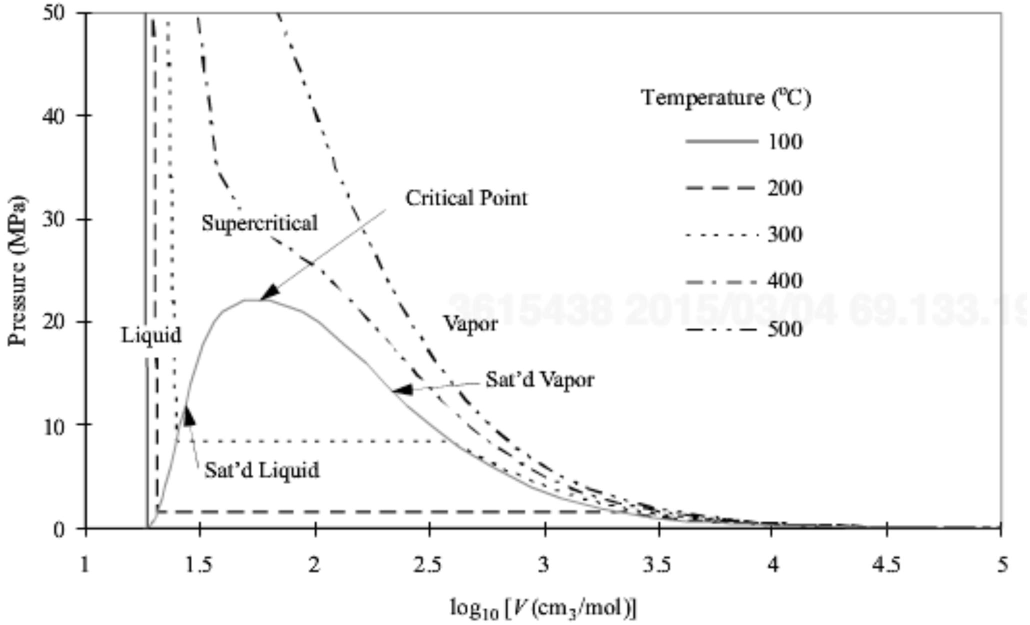


Figure 1.4 *P-V-T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.*

Chemical Potential of an Ideal Gas

-S U V
 H   A
-p G T

$dG = -SdT + VdP$
At constant T
$(dG = Vdp)_T$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp$$

For an ideal gas $V = RT/p$

$\Delta G = RT\ln(p_f/p_i)$ Ideal Gas at constant T, no Enthalpic Interactions

For single component molar $G = \mu$
μ_0 is at $p = 1$ bar
$\mu = \mu_0 + RT \ln p$

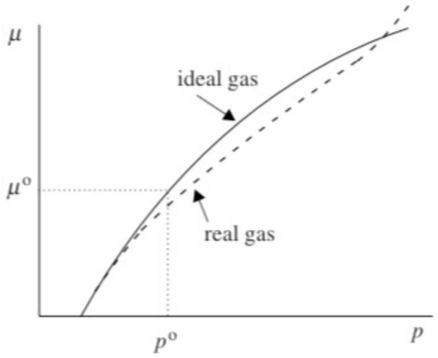


Figure 2.10 Schematic illustration of the pressure dependence of the chemical potential of a real gas showing deviations from ideal gas behaviour at high pressures.

$\mu = \mu_0 + RT \ln p$ i.g.

At equilibrium between two phases the chemical potentials are equal and the **fugacities** of the two phases are also equal.

$$\mu(p) = \mu^{o}(p^{o}) + RT \ln\left(\frac{f}{p^{o}}\right) = \mu^{o} + RT \ln f$$

Real Gas

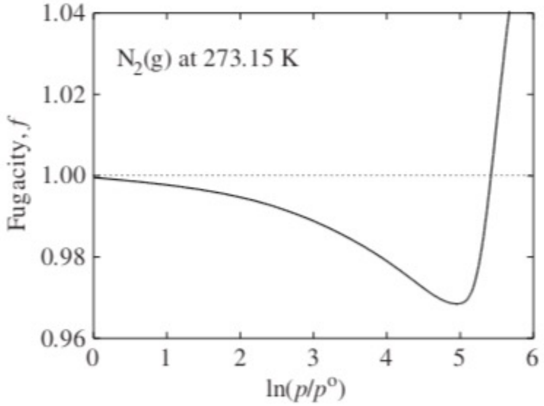


Figure 2.11 Fugacity of $N_2(g)$ at 273.15 K as a function of pressure [15].

$Z = 1$ $\qquad P = RT/V$ $\qquad$ **Ideal Gas Equation of State**

Van der Waals Equation of State

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Cubic Equation of State

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c} \qquad b = \frac{RT_c}{8P_c} \qquad \left(\frac{\partial p}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0$$

Law of corresponding states

$P = RT\rho/(1-b\rho) - a\,\rho^2$

$$Z \equiv \frac{PV}{RT}$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

$$\boxed{Z = 1 + B\rho} + C\rho^2 + D\rho^3 + \ \ldots$$

Virial Equation of State of Onnes

$$B(T) = b - \frac{a}{RT}$$

Peng-Robinson Equation of State (PREOS)

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2} \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a}{bRT}\cdot\frac{b\rho}{1+2b\rho-b^2\rho^2}$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a}{bRT}\cdot\frac{b\rho}{1+2b\rho-b^2\rho^2}$$

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

Cubic Equation of State

Solve cubic equations (3 roots)

Single Component Phase Diagrams

Isochoric phase diagram

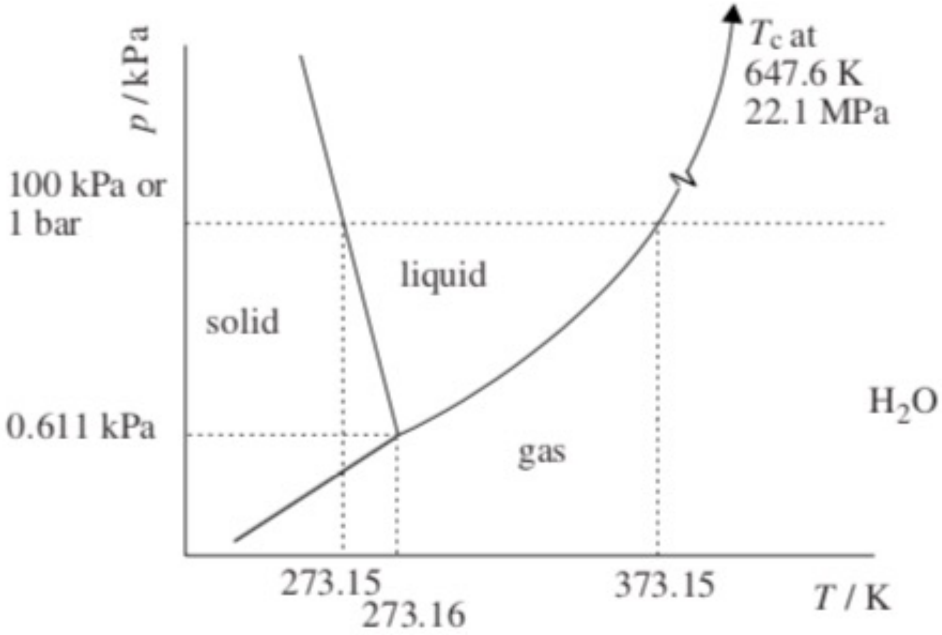


Figure 2.7 The p,T phase diagram of H_2O (the diagram is not drawn to scale).

For a single component, an equation of state relates the variables of the system, PVT

Compound	Tc(K)	Pc(MPa)
METHANE	190.6	4.604

ρ_c = 0.0104 mol/cm³

Gas	T_c (K)	P_c (MPa)
ISOPENTANE	460.4	3.381

ρ_c = 0.00287 mol/cm³

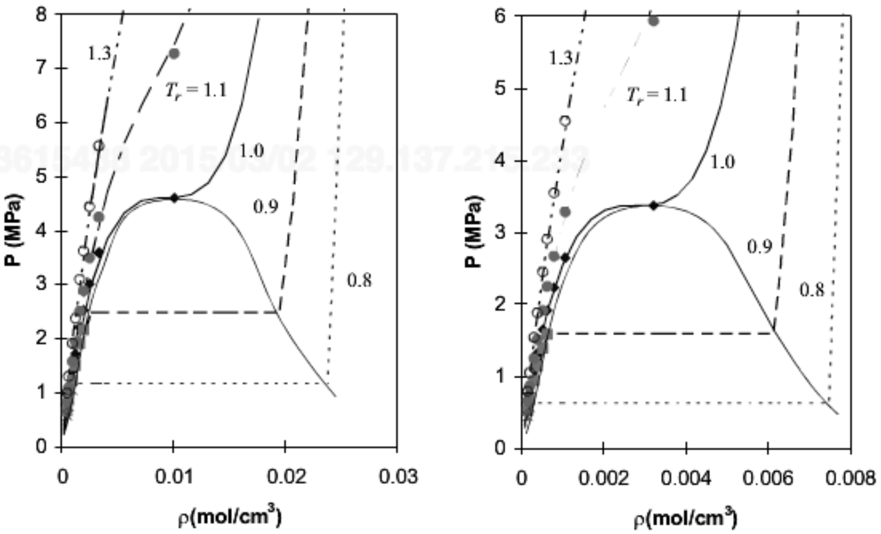


Figure 7.1 *Comparison of the PρT behavior of methane (left) and pentane (right) demonstrating the qualitative similarity which led to corresponding states' treatment of fluids. The lines are calculated with the Peng-Robinson equation to be discussed later. The phase envelope is an approximation sketched through the points available in the plots. The smoothed experimental data are from Brown, G.G., Sounders Jr., M., and Smith, R.L., 1932.* Ind. Eng. Chem., ***24****:513. Although not shown, the Peng-Robinson equation is not particularly accurate for modeling liquid densities.*

At 0.8 * 460.4K = 368K
And 0.64 MPa 2 phases
Higher pressure liquid
Lower vapor

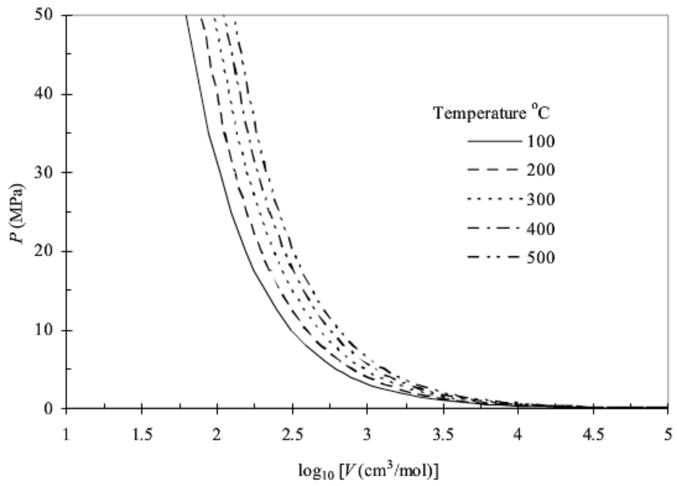


Figure 1.3 *Ideal gas behavior at five temperatures.*

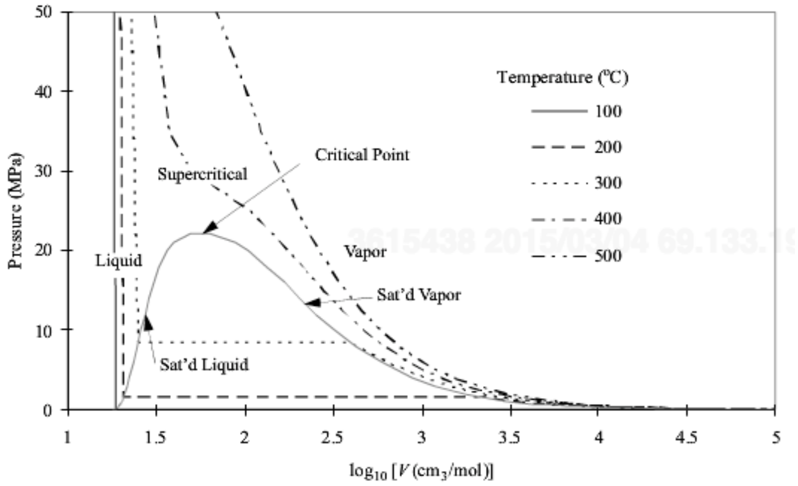


Figure 1.4 *P-V-T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.*

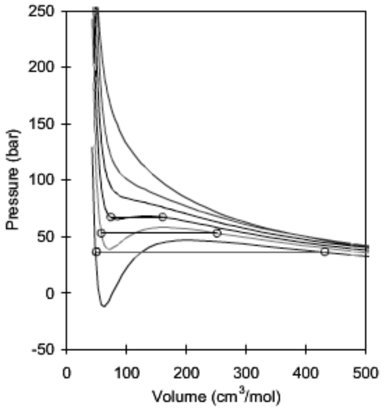


Figure 7.5 *Illustration of the prediction of isotherms by the Peng-Robinson equation of state for CO_2 (T_c = 304.2 K) at 275 K, 290 K, 300 K, 310 K, 320 K, and 350 K. Higher temperatures result in a high pressure for a given volume. The "humps" are explained in the text. The calculated vapor pressures are 36.42 bar at 275 K, 53.2 bar at 290 K, and 67.21 bar at 300 K.*

$$F(Z) = Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{7.25}$$

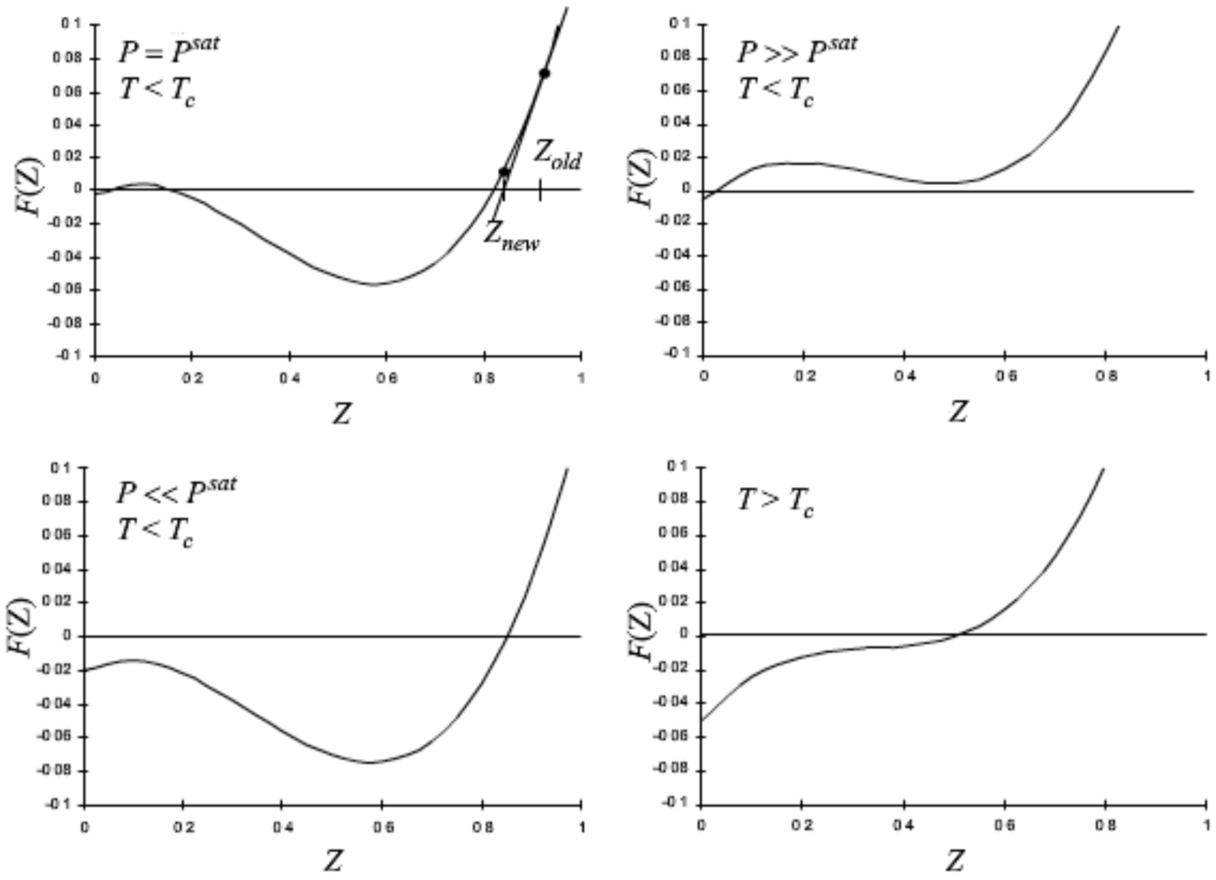


Figure 7.6 *Comparison of behavior of cubic in Z for the Peng-Robinson equation of state at several conditions. The labels Z_{new} and Z_{old} in the upper left are described in the iterative description in Appendix B.*

-S U V
H A
-p G T

CALculation of PHAse Diagrams, CALPHAD

For metal alloys to construct phase diagrams
Calculate the Gibbs Free Energy
Use a Taylor Series in Temperature
Determine the phase equilibria using the chemical potentials
Calculate the derivatives of the free energy expression

$$G_m^o(T) - H_m^{SER} = a + bT + cT\ln(T) + \sum_{n=2}^{i} d_n T^n$$

Get H_m^{SER} from H_m^0 for the components

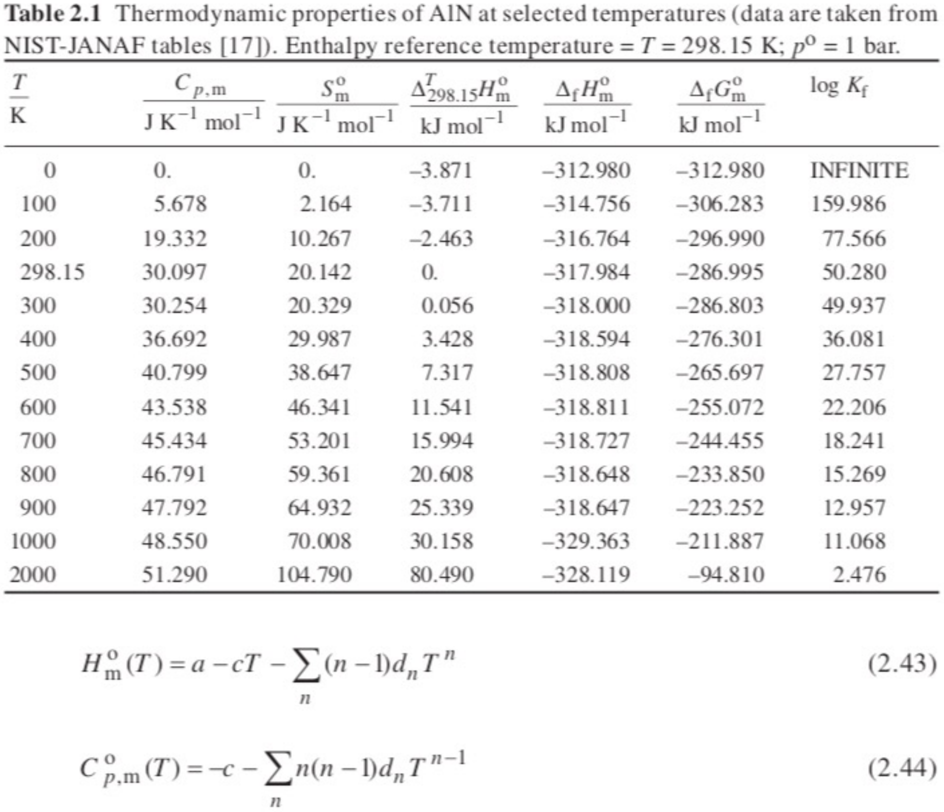


Table 2.1 Thermodynamic properties of AlN at selected temperatures (data are taken from NIST-JANAF tables [17]). Enthalpy reference temperature = T = 298.15 K; p^o = 1 bar.

$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S_m^o}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta_{298.15}^{T}H_m^o}{\text{kJ mol}^{-1}}$	$\frac{\Delta_f H_m^o}{\text{kJ mol}^{-1}}$	$\frac{\Delta_f G_m^o}{\text{kJ mol}^{-1}}$	log K_f
0	0.	0.	–3.871	–312.980	–312.980	INFINITE
100	5.678	2.164	–3.711	–314.756	–306.283	159.986
200	19.332	10.267	–2.463	–316.764	–296.990	77.566
298.15	30.097	20.142	0.	–317.984	–286.995	50.280
300	30.254	20.329	0.056	–318.000	–286.803	49.937
400	36.692	29.987	3.428	–318.594	–276.301	36.081
500	40.799	38.647	7.317	–318.808	–265.697	27.757
600	43.538	46.341	11.541	–318.811	–255.072	22.206
700	45.434	53.201	15.994	–318.727	–244.455	18.241
800	46.791	59.361	20.608	–318.648	–233.850	15.269
900	47.792	64.932	25.339	–318.647	–223.252	12.957
1000	48.550	70.008	30.158	–329.363	–211.887	11.068
2000	51.290	104.790	80.490	–328.119	–94.810	2.476

$$H_m^o(T) = a - cT - \sum_n (n-1) d_n T^n \quad (2.43)$$

$$C_{p,m}^o(T) = -c - \sum_n n(n-1) d_n T^{n-1} \quad (2.44)$$

$$G_{\mathrm{m}}^{\mathrm{o}}(T) - H_{\mathrm{m}}^{\mathrm{SER}}(298.15\ \mathrm{K}) = a + bT + cT\ln(T) + \sum_{n} d_n T^{n}$$

with $H_{\mathrm{m}}^{\mathrm{SER}}(298.15\ \mathrm{K}) = \Delta_0^{298.15} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{FCC\_Al}) = 4540\ \mathrm{J\ mol^{-1}}$.

FCC_Al

$(298.15 < T/\mathrm{K} < 700)$

$-7976.15 + 137.093038\,T - 24.3671976\,T\ln(T) - 1.884662\mathrm{E}^{-3}\,T^{2} - 0.877664\mathrm{E}^{-6}\,T^{3} + 74092\,T^{-1}$

$(700 < T/\mathrm{K} < 933.473)$

$-11276.24 + 223.048446\,T - 38.5844296\,T\ln(T) + 18.531982\mathrm{E}^{-3}\,T^{2} - 5.764227\mathrm{E}^{-6}\,T^{3} + 74092\,T^{-1}$

$(933.473 < T/\mathrm{K} < 2900)$

$-11278.378 + 188.684153\,T - 31.748192\,T\ln(T) - 1.231\mathrm{E}^{28}\,T^{-9}$

Liquid relatively to FCC_Al

$(298.15 < T/\mathrm{K} < 933.473)$

$11005.029 - 11.841867\,T + 7.934\mathrm{E}^{-20}\,T^{7}$

$(933.473 < T/\mathrm{K} < 2900)$

$10482.382 - 11.253974\,T + 1.231\mathrm{E}^{28}\,T^{-9}$

HCP_Al relative to FCC_Al

$(298.15 < T/\mathrm{K} < 2900)$

$5481 - 1.8\,T$

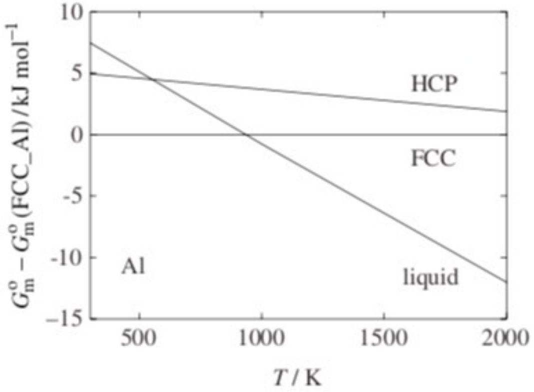


Figure 2.12 $G_{\mathrm{m}}^{\mathrm{o}} - G_{\mathrm{m}}^{\mathrm{o}}(\mathrm{Al\_FCC})$ of hexagonal closed-packed (HCP) aluminium and aluminium melt relative to that of face-centred cubic aluminium [18].