

The Thermodynamics of Phase Transitions

Simple substances exist in three different **phases**: **solid**, **liquid** and **gaseous**. In a P-T diagram we distinguish the **sublimation** line, the **vaporization/condensation** line, and the **melting/freezing** line. The vaporization line terminates at the **critical point**. The point where all three lines meet is called **triple point**. Still, the substance is completely described in P-V-T space by the equation of state.

On all lines two phases coexist, they are also called **two-phase coexistence lines**. This means that for certain combinations of P and T, the equation of state has two solutions with different volume per particle $v=V/N$. In the P-V diagram the isotherm is horizontal at a coexistence state, i.e., for given P there is a whole range of possible V. Since there are only two coexisting phases, the system shows **phase separation** or **phase equilibrium**.

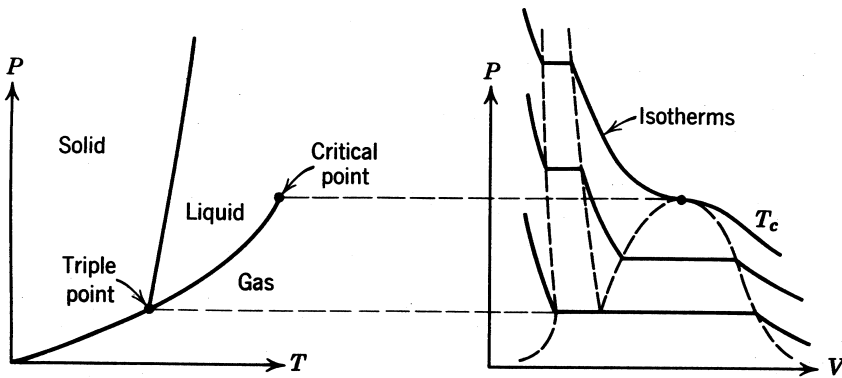
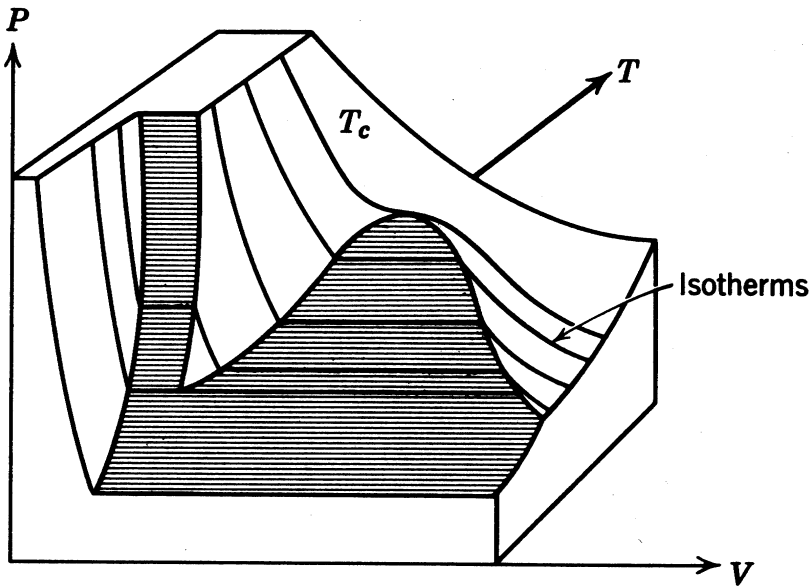
For a given T the pressure at liquid-gas coexistence is called the **vapor pressure**. If the vapor pressure equals the external pressure, the liquid boils (for water, the vapor pressure is 1 bar = 10^5 Pa at 100°C).

Isothermal compression of a pure vapor at coexistence induces condensation, but the pressure stays constant. Only vapor away from coexistence behaves like a normal gas and the pressure rises with compression (this holds for pure substances!).

Upon approach of the critical point, the difference between the liquid and vapor phases disappears.

At the triple point, all three different phases coexist.

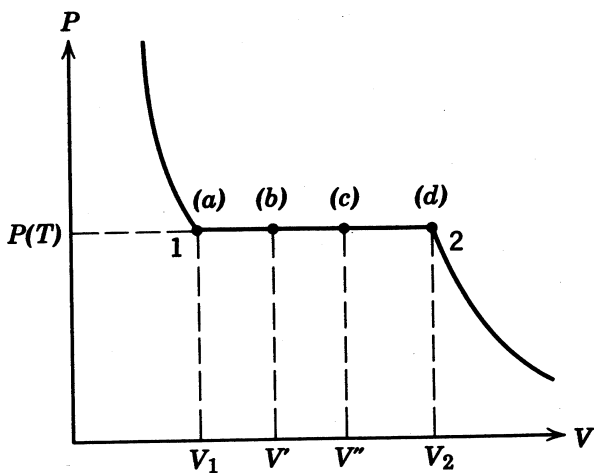
Zustandsgleichung für eine typische Substanz



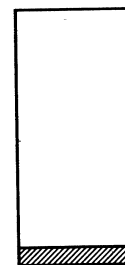
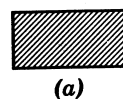
korrespondierende
P-V und
P-T Diagramme

Isotherme mit
Phasenkoexistenz

Diskontinuierlicher
Phasenübergang
bei P und T konstant



nur
flüssig



(a)

(b')

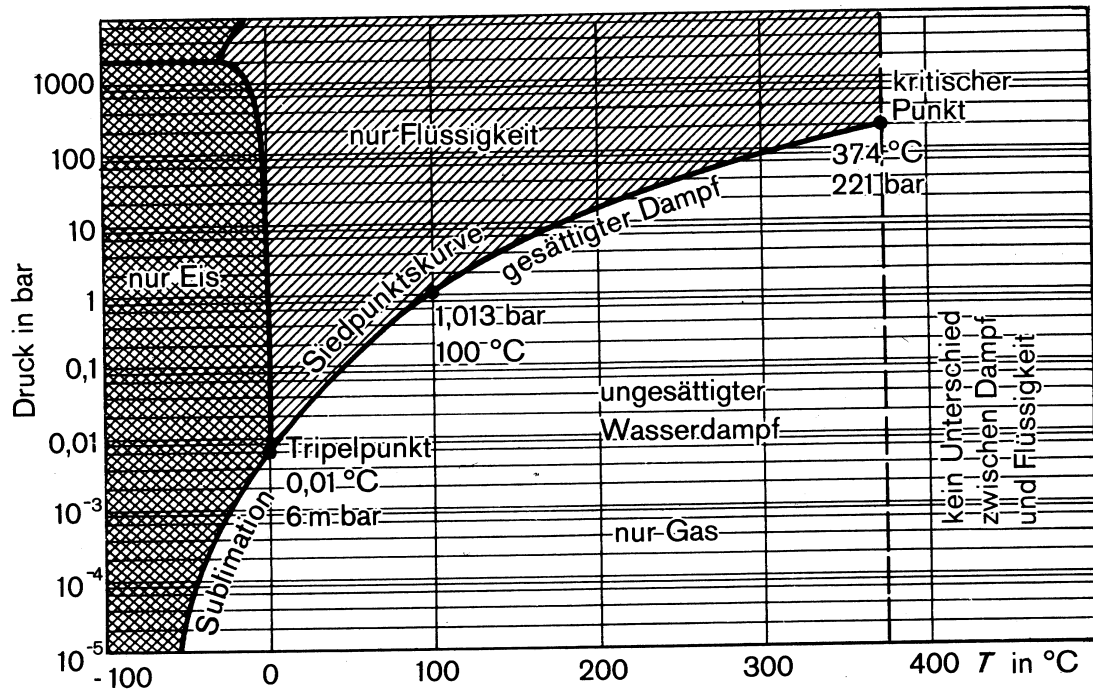
(c)

(d)

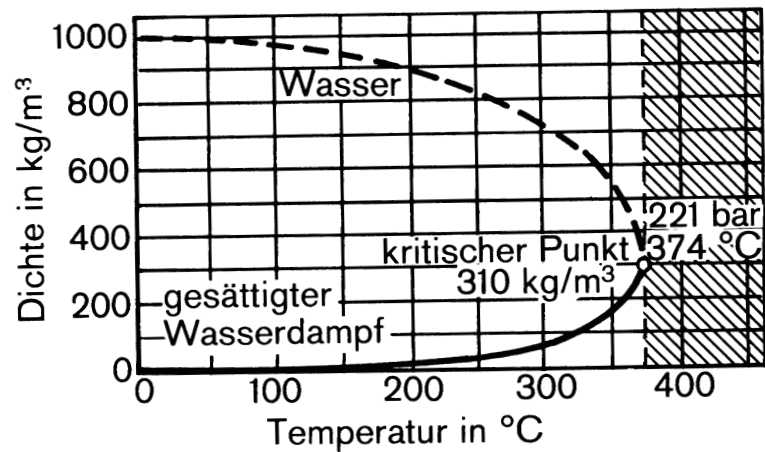
nur
Gas

Phasendiagramm

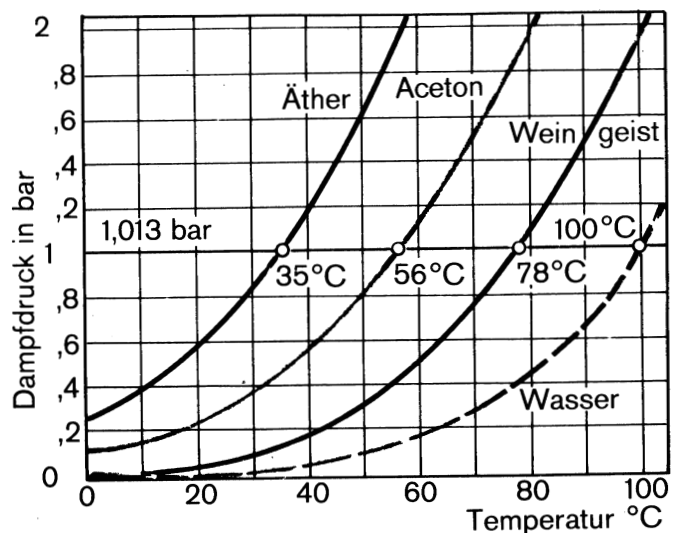
Wasser



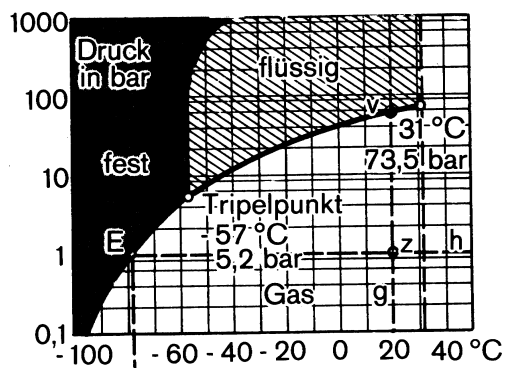
Dichte auf Koexistenzlinie



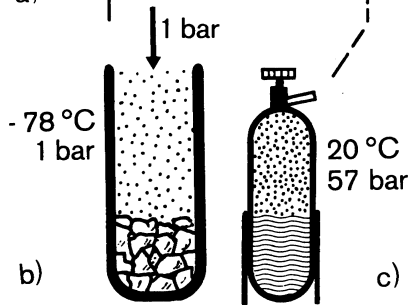
Dampfdruck von verschiedenen Flüssigkeiten



Phasendiagramm und P-V Diagramm von Kohlendioxid

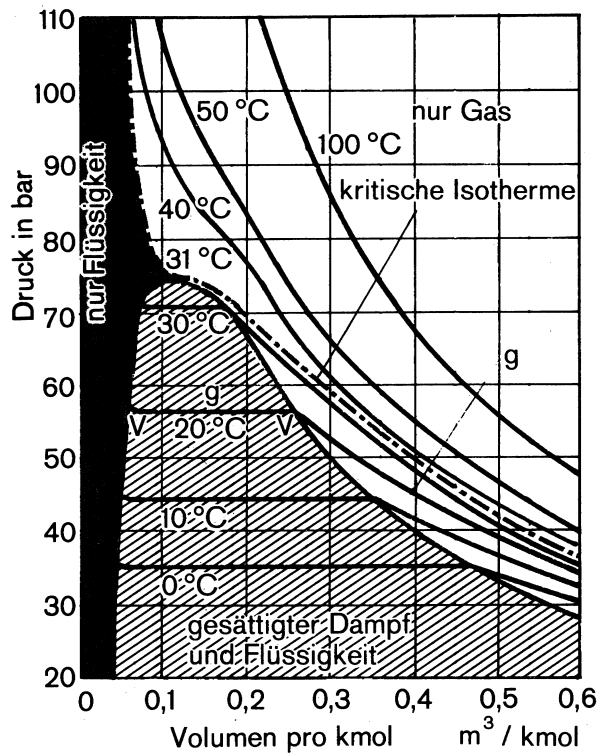


a)



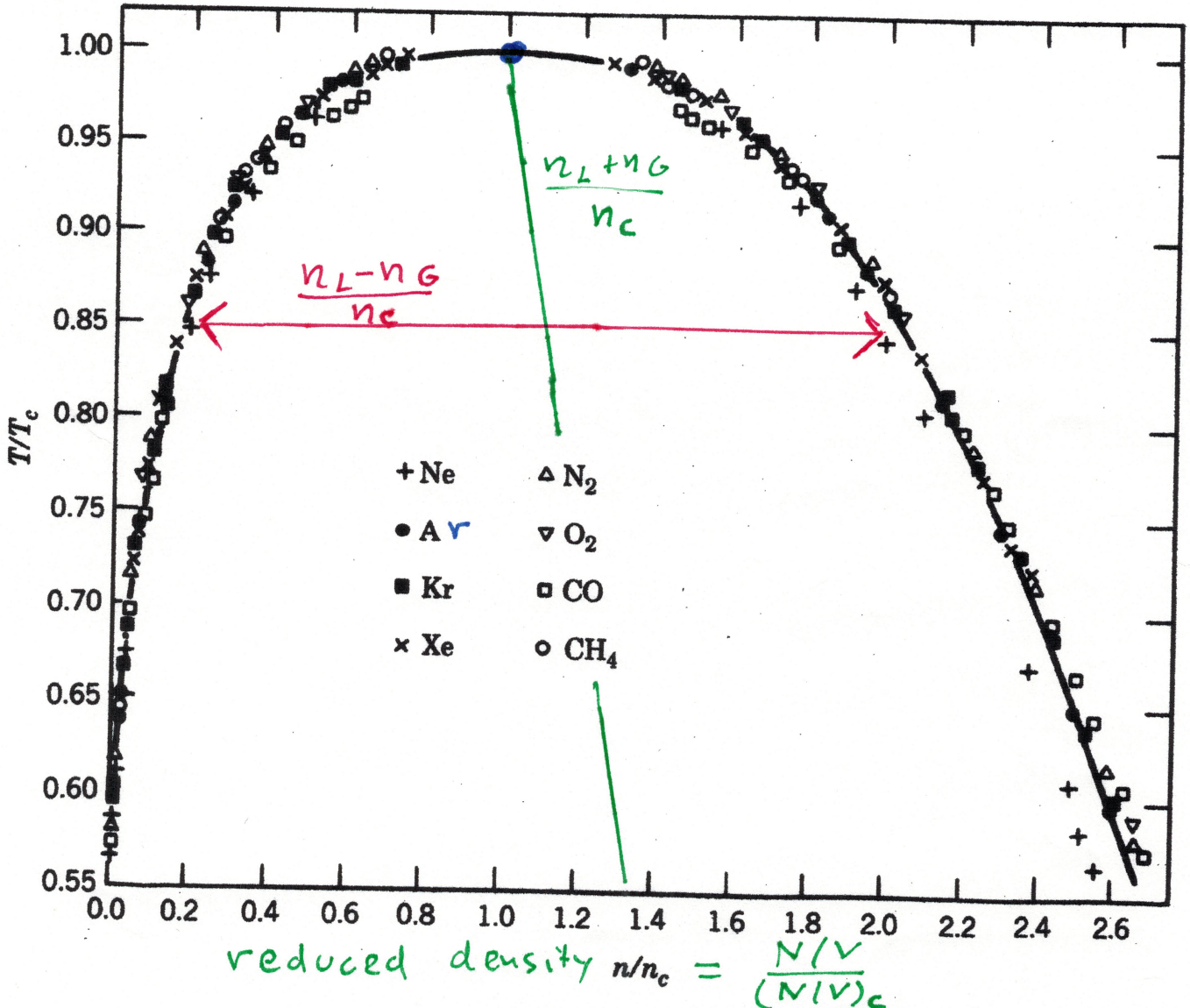
b)

c)



0 0,1 0,2 0,3 0,4 0,5 0,6
Volumen pro kmol m³ / kmol

Hypothese der korrespondierenden Zustände am kritischen Punkt – experimentell bestätigt!



Cyrogenheim's Fit:

$$\frac{n_L + n_G}{n_c} = 1 + \frac{3}{4} (1 - T/T_c)$$

$$\frac{n_L - n_G}{n_c} = \frac{7}{2} (1 - T/T_c)^{1/3}$$

	Ne	Ar	Xe	CO	CH ₄
T _c °C	-229	-122	17	-140	-83
P _c bar	27	49	58	35	46

does not follow from Van-der-Waals equation!