2. Thermodynamics of systems

2.1 The Helmholtz free energy

The only thermodynamic driving force of the changes in the universe is the **increase of entropy**.

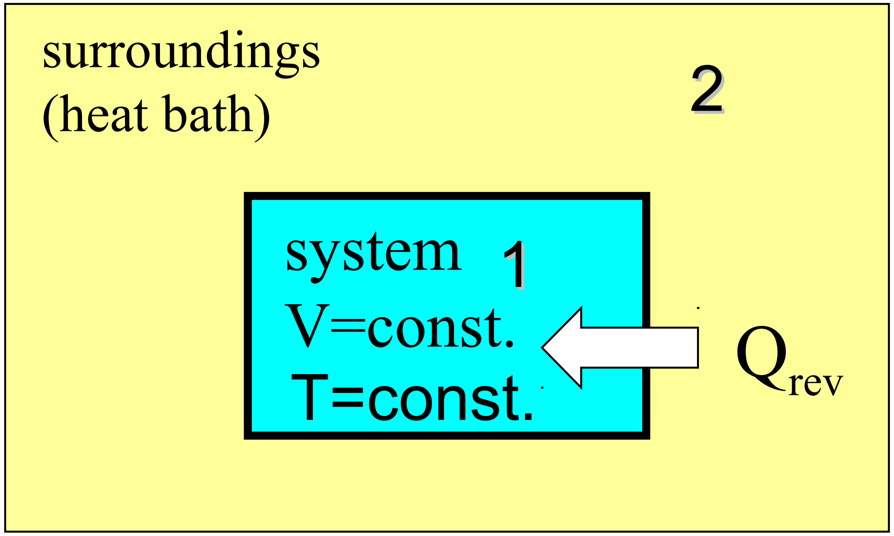
$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0 \qquad (1.78)$$

We define two further thermodynamic functions which are suitable for describing processes in closed but not isolated systems.

Constant T and V: ***Helmholtz free energy (A)***
Constant T and p: ***Gibbs free energy (G)***

Constant T and V:

Fig. 2.1



(E.g. a closed flask in which a slow process is taking place)

The only interaction with the surroundings is the Q heat exchange.

$$\Delta S_1 + \Delta S_2 \geq 0 \quad \Delta S_2 = -\frac{Q_{rev}}{T}$$

Negative since it is defined for the system: system gain.

$$\Delta S_1 - \frac{Q_{rev}}{T} \geq 0 \cdot (-T)$$

$$Q_{rev} - T\Delta S_1 \leq 0$$

At constant volume: $Q_{rev} = \Delta U_1$. Leave out the subscript 1:

$$\Delta U - T \cdot \Delta S \leq 0 \qquad (2.1)$$

$$\Delta U - T \cdot \Delta S \leq 0$$

*So we can define a **function** which decreases in **isothermal-isochor** processes and has a minimum at equilibrium.*

$$\boxed{A = U - TS} \qquad (2.2)$$

*In closed systems the direction of **isothermal-isochor processes and the equilibrium** can be expressed as follows:*

$$\boxed{\begin{array}{ll} \Delta A_{T,V} \leq 0 & \text{(no work done)} \\ dA_{T,V} \leq 0 & \text{(no work done)} \end{array}} \qquad (2.3)$$

*In a closed system of constant temperature and volume (if no work is done) the **Helmholtz free energy** decreases in a spontaneous process and has a minimum at equilibrium.*

The differential expression of Helmholtz free energy:

$$dA = dU - TdS - SdT \qquad dU = -pdV + TdS$$

$$\boxed{dA = -pdV - SdT} \qquad (2.4)$$

The change of Helmholtz free energy in an isothermal reversible process is equal to the ***work****. We can prove this in the following way:*

Write the differential expression of Helmholtz free energy,

keep T constant, allow other than pV work, too.

$$dA_T = dU - TdS - \cancel{SdT} \qquad TdS = \delta Q_{rev}$$

$$dA_T = dU - \delta Q_{rev} \qquad dU = \delta W_{rev} + \delta Q_{rev}$$

$$\boxed{\begin{aligned} dA_T &= \delta W_{rev} \\ \Delta A_T &= W_{rev} \end{aligned}} \qquad (2.5)$$

This is why A is sometimes called the work function. Arbeit = work (in German)

Why „free" energy ?

„bound" energy (cannot be converted to work)

$$U = A + TS$$

2.2 Gibbs free energy (G)

It describes systems ,which are in thermal and mechanical interaction with the surroundings ($T_1 = T_2$, $p_1 = p_2$).

$$\Delta S_1 + \Delta S_2 \geq 0 \qquad \Delta S_2 = -\frac{Q_{rev}}{T}$$

$$\Delta S_1 - \frac{Q_{rev}}{T} \geq 0 \qquad \cdot(-T)$$

$$Q_{rev} - T\Delta S_1 \leq 0 \qquad Q_{rev} = \Delta H_1$$

(at constant pressure if no other work is done)

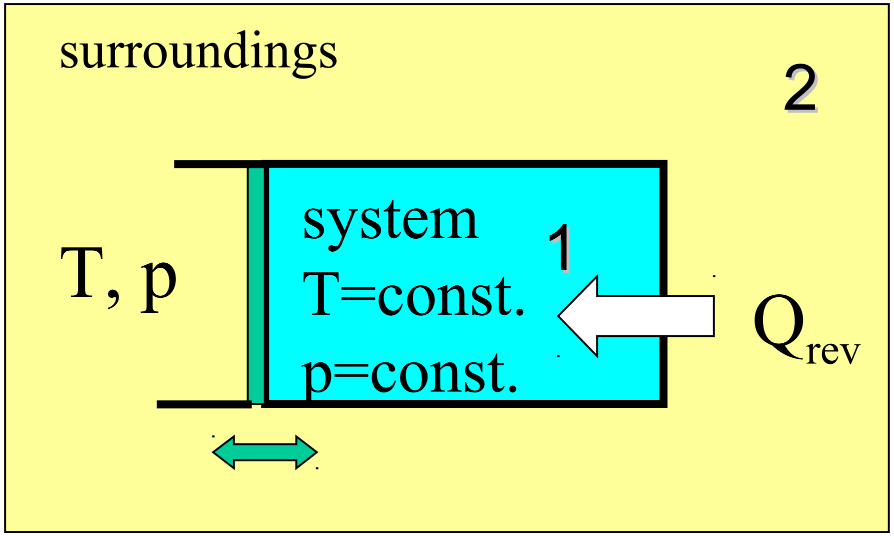


Fig. 2.2

$$\Delta H - T \cdot \Delta S \leq 0 \qquad (2.6)$$

The Gibbs free energy: $\boxed{G = H - TS}$ (2.7)

$$\boxed{\begin{array}{ll} \Delta G_{T,p} \leq 0 & \text{(no other than pV work)} \\ dG_{T,p} \leq 0 & \text{(no other than pV work)} \end{array}}$$ (2.8)

In a closed system of constant temperature and pressure, if no other than pV work is done, the ***Gibbs free energy decreases in a spontaneous process****, and it has a minimum at equilibrium.*

The relationship between G and A

$$G = H - TS = \underbrace{U + pV - TS}_{} = A + pV \qquad (2.9)$$

In differential form: $dG = dU + pdV + Vdp - TdS - SdT$ (2.10)

If there is pV work only : $dU = -pdV + TdS$

$$\boxed{dG = Vdp - SdT} \qquad (2.11)$$

At constant temperature and pressure (in a reversible process), if there is no other than pV work:

$$\boxed{dG_{p,T} = 0} \qquad (2.12)$$

If there is other (non-pV) work:

$$dU = \delta W_{other} - pdV + TdS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$\boxed{dG_{p,T} = \delta W_{other}} \qquad (2.13a)$$

$$\boxed{\Delta G_{p,T} = W_{other}} \qquad (2.13b)$$

In an isothermal, isobaric reversible process the change of Gibbs free energy is equal to the non-pV work.

*The **chemical potential** of a pure substance (J/mol)*

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} \qquad (2.14)$$

2.3. The first and second derivatives of the thermodynamic functions

Useful relationships can be obtained from the four thermodynamic functions (U, H, A, G) by partial derivation.

The relations between the second derivatives are called Maxwell relations.

The result is independent of the order of derivation., for example:

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \qquad (2.15)$$

$\boxed{U}$ $$\boxed{dU = -pdV + TdS} \tag{2.16a}$$

The first derivatives:

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \qquad \left(\frac{\partial U}{\partial S}\right)_V = T \tag{2.16b}$$

The second derivatives:

$$\left(\frac{\partial^2 U}{\partial V \partial S}\right) = -\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \tag{2.16c}$$

$$\boxed{H}$$

$$H = U + pV \quad dH = dU + pdV + Vdp$$

$$dU = -pdV + TdS \qquad \boxed{dH = Vdp + TdS} \tag{2.17a}$$

The first derivatives:

$$\left(\frac{\partial H}{\partial p}\right)_S = V \qquad \left(\frac{\partial H}{\partial S}\right)_p = T \tag{2.17b}$$

The second derivatives:

$$\left(\frac{\partial^2 H}{\partial p \partial S}\right) = \left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \tag{2.17c}$$

A

$$\boxed{dA = -pdV - SdT} \qquad (2.18a)$$

The first derivatives:

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \qquad (2.18b)$$

The second derivatives:

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = -\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

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

(2.18c)

The S-V functions can be determined from measurable quantities (see 2.18c)

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT_V + \left(\frac{\partial V}{\partial p}\right)_T dp_V = 0$$

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

Isothermal compessibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

thermal expansion coeff.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{G}$$

$$\boxed{dG = Vdp - SdT} \tag{2.19a}$$

The first derivatives:

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S \tag{2.19b}$$

The second derivatives:

$$\left(\frac{\partial^2 G}{\partial p \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p} = -V\alpha \tag{2.19c}$$

The S –p functions can be determined from measurable quantities

*The pressure dependence of **enthalpy** at constant temperature*

$$\mathrm{H = G + TS}$$

Derive with respect to T!

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial G}{\partial p}\right)_T + T\left(\frac{\partial S}{\partial p}\right)_T$$

See 2.19b

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \qquad (2.20)$$

Using this formula we can prove that the enthalpy of an ideal gas is independent of pressure (at constant temperature).

General relation between C_{mp} and C_{mv}

H=U+pV

$$C_{mp}-C_{mV}=\frac{1}{n}\left(\left(\frac{\partial H}{\partial T}\right)_p-\left(\frac{\partial U}{\partial T}\right)_V\right)=\frac{1}{n}\left(\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p-\left(\frac{\partial U}{\partial T}\right)_V\right)$$

p=const., i.e., p and V not independent

$$dU_p=\left(\frac{\partial U}{\partial T}\right)_V dT_p+\left(\frac{\partial U}{\partial V}\right)_T dV_p \quad\xrightarrow[:dT_p]{}\quad \left(\frac{\partial U}{\partial T}\right)_p=\left(\frac{\partial U}{\partial T}\right)_V+\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

U=U(V,T)

$$C_{mp}-C_{mV}=\frac{1}{n}\left(\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p\right)=\frac{1}{n}\left(\left(\frac{\partial U}{\partial V}\right)_T+p\right)V\alpha$$

See 2.18c

$$dU_T=-pdV_T+TdS_T \quad\Longrightarrow\quad \left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial S}{\partial V}\right)_T-p=T\left(\frac{\alpha}{\kappa_T}\right)-p$$

$$\boxed{C_{mp}-C_{mV}=\frac{1}{n}\frac{VT\alpha^2}{\kappa_T}}$$

Thermodynamic functions of state

(Closed system, pV work only)

Internal energy: $U = W + Q$ $\Delta U = Q_V$ (2.21a)

Enthalpy: $H = U + pV$ $\Delta H = Q_p$ (2.21b)

Helmholtz function: $A = U - TS$ $\Delta A_{T,V} \leq 0$ (2.21c)

Gibbs function: $G = H - TS$ $\Delta G_{T,p} \leq 0$ (2.21d)

Thermodynamic functions of state

$$H = U + pV$$

$$A = U - TS$$

$$G = H - TS$$

A is the smallest

$$U = A + TS$$

$$G = A + pV$$

$$H = U + pV = A + TS + pV$$

H is the largest

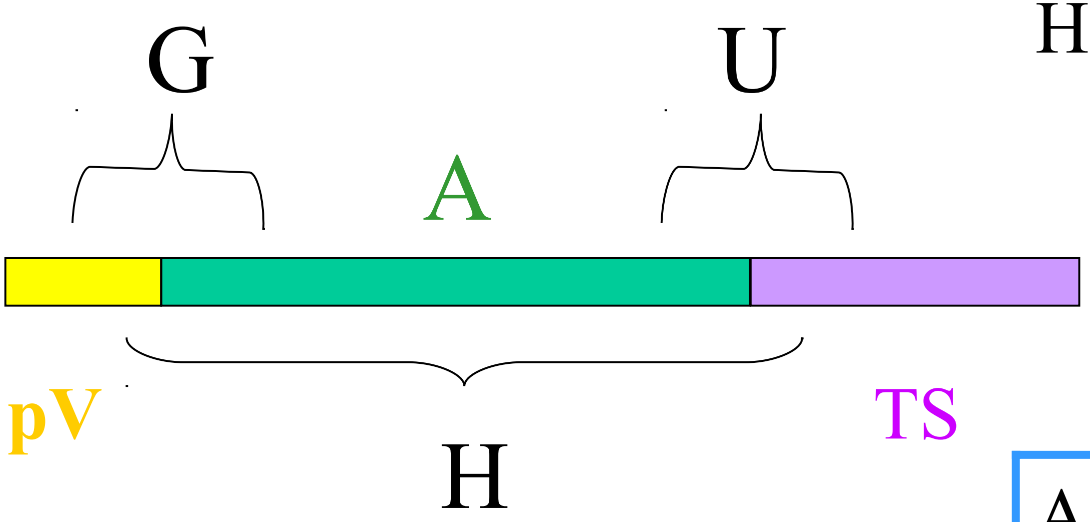


Fig. 2.3

$$\boxed{A < G < U < H} \qquad (2.22)$$

2.4. p-T phase diagram

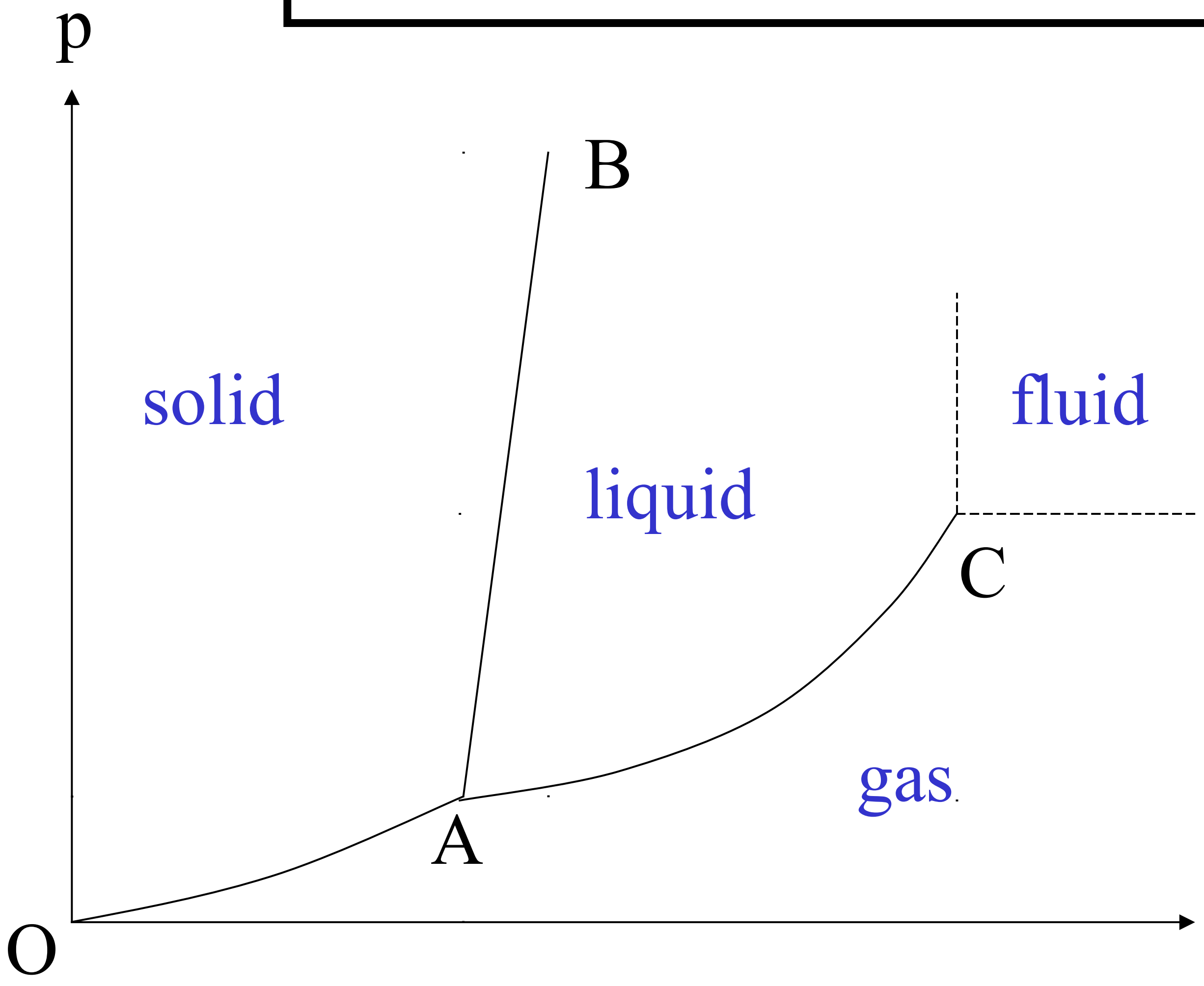


Fig. 2.4

OA: subl. curve

AB: melting curve

AC: vaporization curve

A: triple point

C: critical point

Solid → liquid **melting** positive slope (except for water)

Solid →gas **sublimation**

Liquid → gas **boiling**

Equilibrium of two phases, p and T are not independent

A*:triple point, three phases are in equilibrium. Its temperature and pressure are characteristic of the substance.*

E.g. Water: 6.11 mbar, 273.16K

CO_2: 5.11 bar, 216.8K

Dry ice snow falling on Mars (2006-2007, NASA's Mars Reconnaissance Orbiter)

At atmospheric pressure CO_2 *does not exist in liquid state.*

C: **critical point:** *The difference between liquid and vapor phase diminishes.*

At greater temperatures and pressures only one phase exists: ***fluid (supercritical) state***.

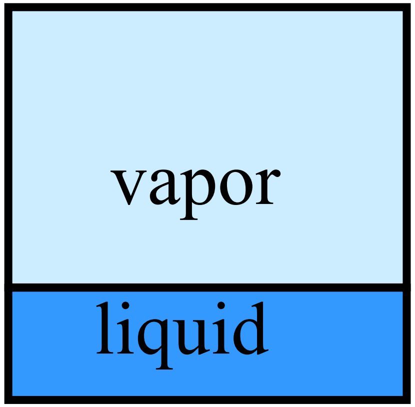


Fig. 2.5

Let us heat a liquid-vapor system in a vessel of an appropriate volume. (We are going from left to right on the vapor pressure curve.) It can be observed:

The density of the liquid decreases.
The density of the vapor increases.

Other physical properties (e.g. refractive index) also approach each other. Finally we reach to a point where the difference between the two phases diminishes
→ ***critical point.***

Critical temperature, *above which the gas cannot be liquefied*

Critical pressure, *what is necessary to liquefy the gas at the critical temperature yet.*

Critical volume, *what 1 mol gas occupies at the critical pressure and temperature*

The critical data are characteristic of the substance.

Examples:

Water: $T_C = 647.4$ K, $p_C = 221.2$ bar

CO_2: $T_C = 304.2$ K, $p_C = 73.9$ bar

T_C below room temperature: O_2, N_2, CO, CH_4

These gases cannot be liquefied at room temperature.

T_C above room temperature : CO_2, NH_3, Cl_2, C_3H_8

These gases can be liquefied at room temperature

2.5 Thermodynamic interpretation of the p-T diagram (the Clapeyron equation)

At given T and p the condition of equilibrium is the minimum of G.

One component, two phases (a and b)

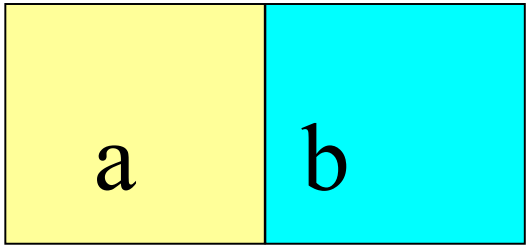


Fig. 2.6

At equilibrium the molar Gibbs free energy of the component must be equal in the two phases. Otherwise there is a flow of the substance from the phase where $G_m=G/n$ is higher to the phase where G_m is lower.

Three cases:

1. $G_m^a > G_m^b$: substance goes from a to b
2. $G_m^a < G_m^b$: substance goes from b to a
3. $G_m^a = G_m^b$: equilibrium

1, 2: Macroscopic process takes place

3: No macroscopic process

On the molecular level there are changes. The rates of the processes in opposite direction are the same (e.g. in liquid vapor equilibrium the **macroscopic** rates of evaporation and of condensation are equal).

The equilibrium is **dynamic** (and not static), **fluctuation** occurs.

Derivation of the Clapeyron equation:

$$G_m^a = G_m^b \quad \text{(equilibrium)} \qquad (2.23)$$

If we change *T* slightly, *p* and *G* also change.

The condition of maintaining equilibrium:

$$dG_m^a = dG_m^b \qquad dG = Vdp - SdT$$

$$V_m^a dp - S_m^a dT = V_m^b dp - S_m^b dT$$

$$(V_m^b - V_m^a)dp = (S_m^b - S_m^a)dT \qquad (2.24)$$

$$V_m^b - V_m^a = \Delta V_m \qquad S_m^b - S_m^a = \Delta S_m$$

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} \qquad \Delta S_m = \frac{\Delta H_m}{T}$$

$$\frac{\mathrm{dp}}{\mathrm{dT}} = \frac{\Delta \mathrm{H_m}}{\mathrm{T} \cdot \Delta \mathrm{V_m}} \tag{2.24}$$

*This is the **Clapeyron equation** (the equation of one component phase equilibrium).*

Nothing was neglected in the derivation.

It is valid for: liquid-vapor
solid-liquid
solid-vapor
solid-solid equilibrium

We can obtain the **curves of the p-T diagram** by integration of the Clapeyron equation. For exact integration ΔH_m and ΔV_m have to be known as functions of temperature.

Qualitative interpretation: $\frac{dp}{dT}$ is the slope of the curve.

1. The melting point curve is the steepest

Reason: ΔV_m is small (and it is in the denominator)

2. Near the triple point the sublimation curve is steeper than the boiling point curve.

Reason:

$$\Delta H_{m,subl} = \Delta H_{m,fus} + \Delta H_{m,evap} \qquad (2.25)$$

ΔV_m (sublimation) is roughly the same ($\approx V_m$(vapor))

3. In most cases the melting point curve has a positive slope because ΔV_m is positive (the substance expands at melting).

Exception: water, $\Delta V_m = V_m(l) - V_m(s) < 0$, see the figure below (water contracts until 4 °C)

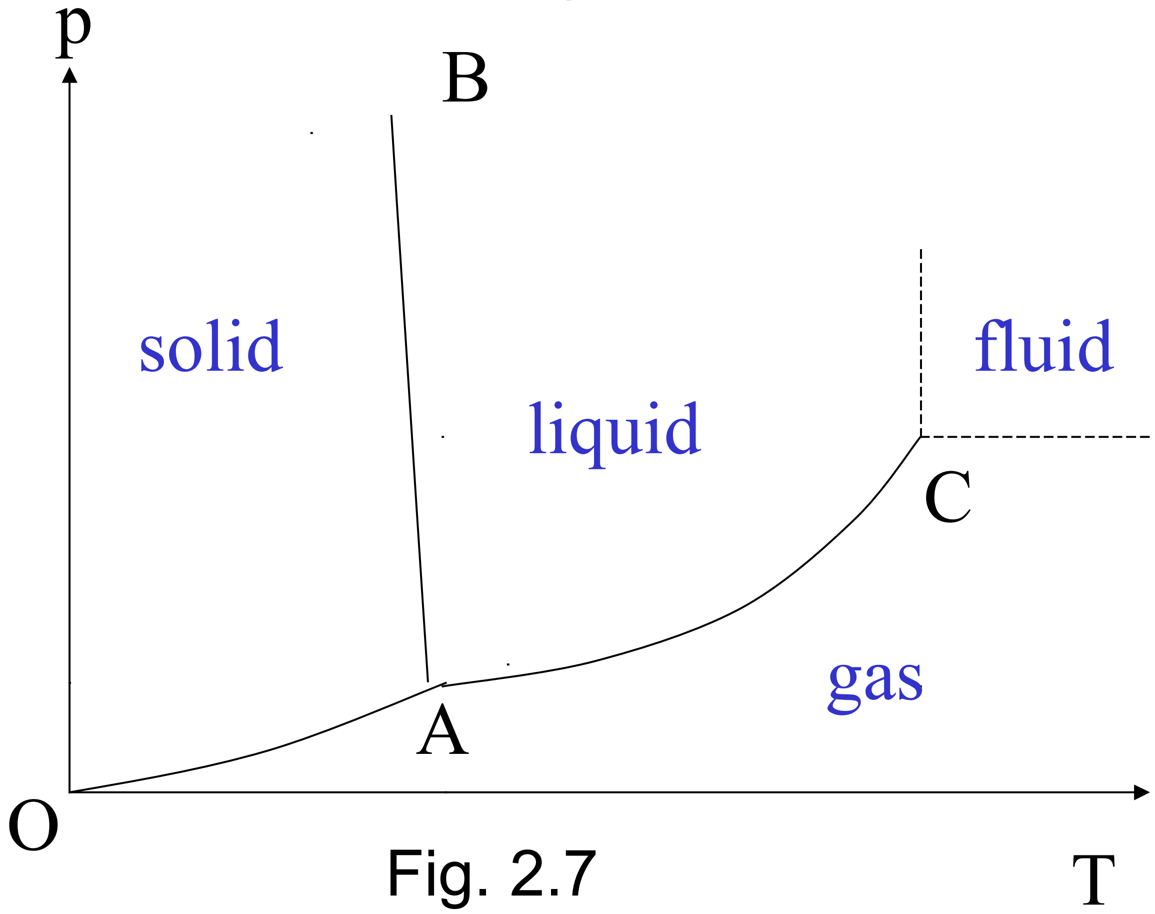


Fig. 2.7

The slope of AB is negative.
Melting point decreases as the pressure increases (operation of ice-skate).

2.6.One component liquid-vapor, solid-vapor equilibria, the Clapeyron Clausius equation

Experience:The vapor pressure of a pure liquid depends on temperature only.

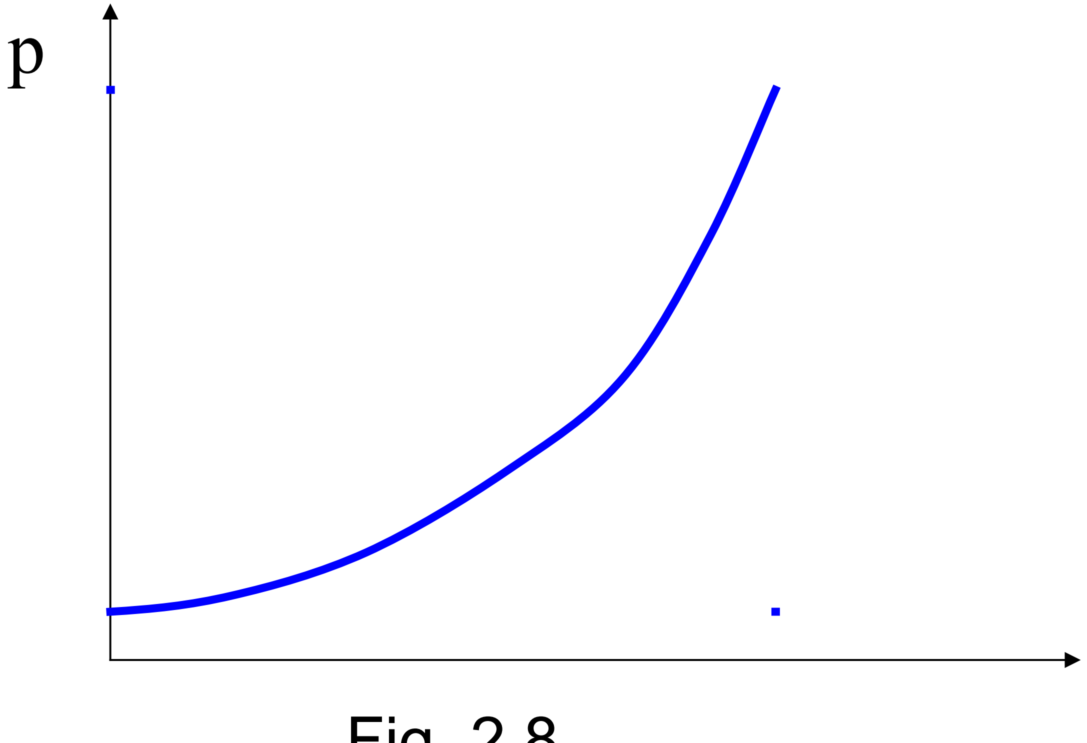


Fig. 2.8

Exponential-like function

If the logarithm of the vapor pressure is plotted against the reciprocal of temperature, we obtain a straight line:

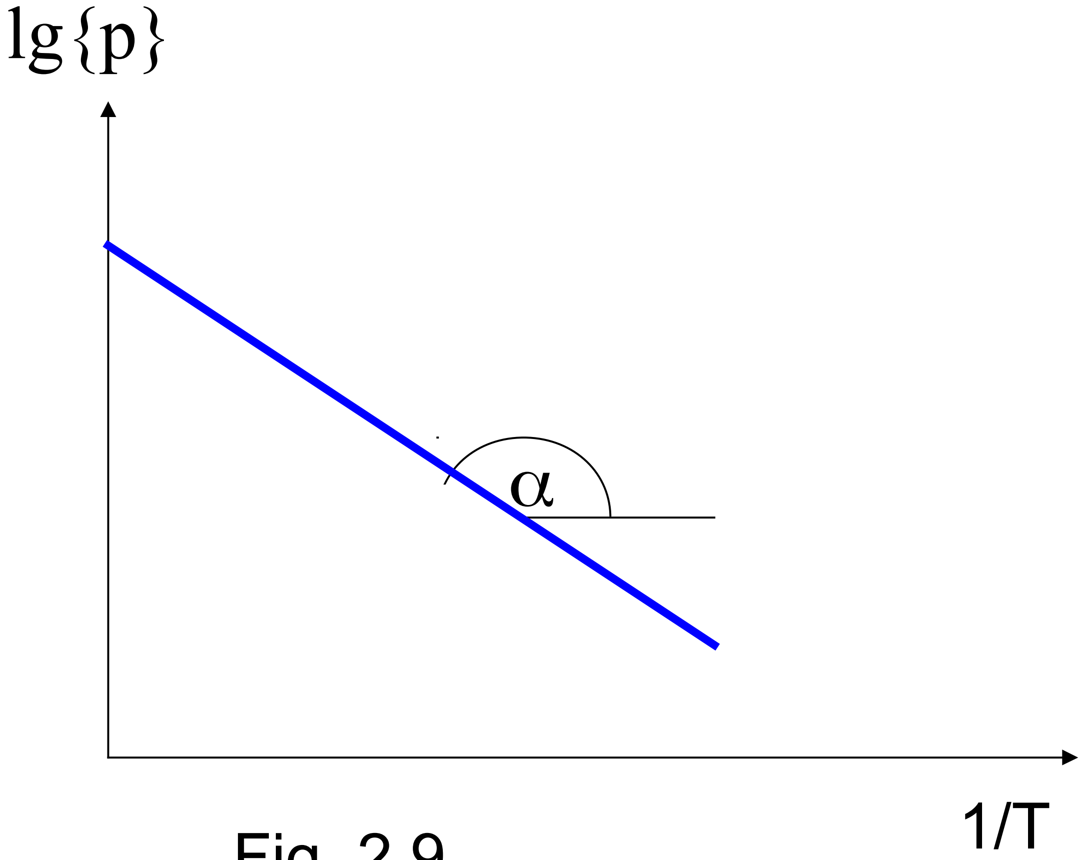


Fig. 2.9

$$\lg\{p\} = -\frac{A}{T} + B \qquad (2.26)$$

A, B: constants

$$\tan\alpha = -A$$

$$\{p\} = \frac{p(Pa)}{1\,Pa}$$

The derivation of the Clapeyron Clausius equation

Apply the Clapeyron equation for liquid-vapor equilibrium

$$\frac{dp}{dT}=\frac{\Delta H_m}{T\cdot\Delta V_m}$$

molar heat of vaporization

change of molar volume at vaporization

1. step: We neglect the molar volume of the liquid (compared to vapor),

2. step: We regard the vapor as ideal gas.

Therefore $$\Delta V_m \approx V_m(g)=\frac{RT}{p}$$

3. step ΔH_m will be denoted by λ and ***regarded independent of temperature***

$$\frac{dp}{dT} = \frac{\lambda \cdot p}{RT^2} \longrightarrow \frac{dp}{p} = \frac{\lambda}{R} \cdot \frac{dT}{T^2} \qquad (2.27)$$

dp/p = dlnp, because dlnp/dp = 1/p (derivative of ln p)

$dT/T^2 = -d(1/T)$, because $d(1/T)/dT = -1/T^2$

$$d \ln p = -\frac{\lambda}{R} d\left(\frac{1}{T}\right)$$

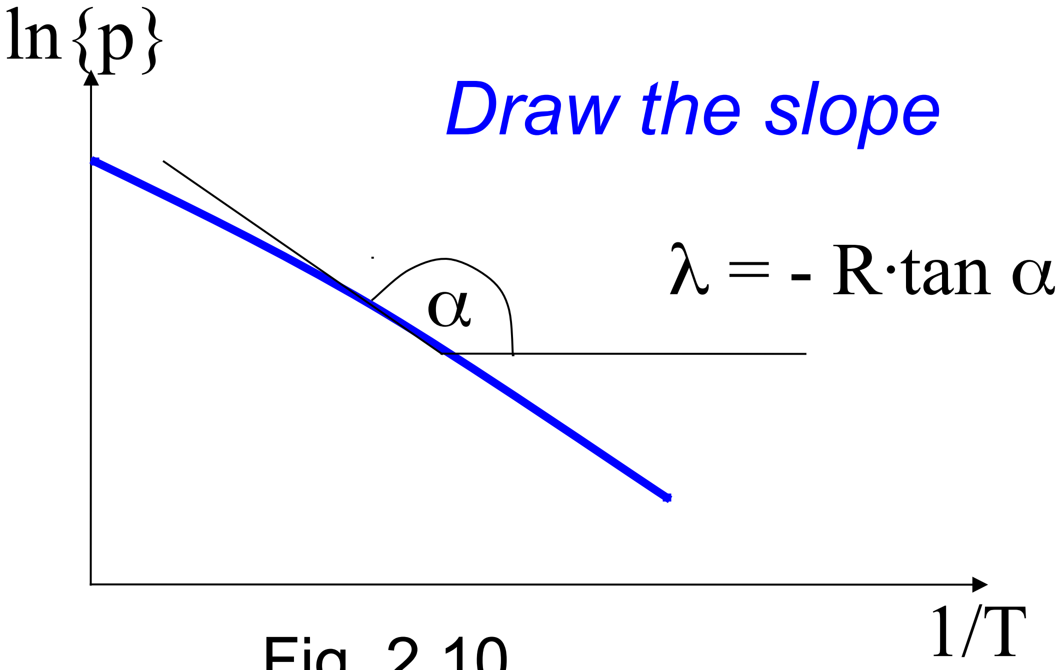
A

$$\lambda = -R \frac{d \ln p}{d\left(\frac{1}{T}\right)}$$

B

λ is taken independent of T in following integration

A) *Determination of λ from ln{p}-1/T diagram*



Draw the slope

$\lambda = - R \cdot \tan \alpha$

$$\ln\{p\} = -\frac{\lambda}{RT} + C$$

Fig. 2.10

B) *Integration (λ is taken independent of T)*

(2.28)

Empirical formula: $\lg\{p\} = -\frac{A}{T} + B$ (2.29)

Integration between limits: (2.30)

$$\ln p_2 - \ln p_1 = -\frac{\lambda}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \ln\frac{p_2}{p_1} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$T_1, p_1, T_2, p_2, \lambda$:

if one parameter is unknown, it can be calculated .

This Clapeyron Clausius equation contains ***two constants****.*

There are ***other empirical equations****, too, for extending the linearity of the ln p – 1/T equation: One of them is the*

Antoine equation:

$$\lg\{p\} = A - \frac{B}{T + C} \qquad (2.31)$$

It contains ***three constants****.*

2.7 Standard Gibbs free energies

The Gibbs free energies are significant in calculation of chemical equilibria.

*The **standard states are fixed** (similarly to enthalpies) by international conventions:*

Gas: *ideal gas at p^0 (10^5 Pa) pressure (fictitious)*
Liquid: *pure liquid at p^0 pressure*
Solid: *the most stable crystal state at p^0 pressure*

For elements in standard state: $H_m^0(298\,K)=0$

At standard pressure the gases are real gases, the enthalpies of gaseous elements are not exactly zero.

Standard state of gaseous elements

To obtain the molar enthalpies of real gas of elements, a hypothetical process is considered.

In an isothermal process the ideal gas is expanded to zero pressure, switched on the interactions, then the real gas is compressed back to 1 bar.

$$H_{m,real}^{298\,K}\left(p^0\right)=H_{m,real}^{298\,K}\left(p^0\right)-H_{m,ideal}^{298\,K}\left(p^0\right)=$$

$$\underbrace{\int_{p^0}^{0}\left(\frac{dH_m}{dp}\right)_{T=298\,K\,,ideal}dp}_{=0,\,H_{ideal}=H_{ideal}(T)}+\underbrace{\Delta H_{0\,\text{bar}\,,\,\text{switch on the interactions}}}_{0}+\int_{0}^{p^0}\left(\frac{dH_m}{dp}\right)_{T=298\,K\,,\,real}dp=$$

$$\left(\frac{dH}{dp}\right)_T=\left(\frac{dG}{dp}\right)_T+T\left(\frac{dS}{dp}\right)_T=V-T\left(\frac{dV}{dT}\right)_p$$

$$\boxed{H_{m,real}^{298\,K}\left(p^0\right)=\int_{p^0}^{0}\left[V_m-T\left(\frac{dV_m}{dT}\right)_p\right]dp}$$

It is a small negative correction, e.g.,

Ar:	-7 J/mol
Kr:	-17 J/mol
N_2:	-6 J/mol
C_2H_6:	-61 J/mol

Notation of standard state: ^{0} as superscript.

In the definition of Gibbs free energy both ***enthalpy*** *and* ***entropy*** *take part: $G = H - TS$*

Remember: The zero level of entropy is fixed by the third law of thermodynamics: the entropy of pure crystalline substance is zero at zero K (subsection 1.18)

By convention:

At ***298,15 K*** *(25 ^{o}C) and* ***$p^o = 10^5$ Pa*** *pressure the enthalpy of an element in standard state is taken zero (for gases it fictitious), that of a compound is taken equal to the enthalpy of formation.*

We do not use a similar convention for G but we calculate it from H and S.

The standard molar Gibbs free energy is

$$G_m^0 = H_m^0 - T \cdot S_m^0 \qquad (2.32)$$

So the standard molar Gibbs free energy of the elements at 298 K is not zero.

Standard Gibbs free energy of formation*: the Gibbs free energy change of the reaction, in which the compound is formed from its elements so that all the reactants are in their standard state. It is denoted by* $\Delta_f G^0$.

Standard Gibbs free energy of reaction, $\Delta_r G^0$.

$$\Delta_r G^0 = \Sigma \nu_B G^0_{mB} - \Sigma \nu_A G^0_{mA} \qquad (2.33)$$

Or from standard Gibbs free energies of formation: at any temperature

$$\Delta_r G^0 = \Delta_r (\Delta_f G^0) \qquad (2.34)$$

Example $2SO_2 + O_2 = 2SO_3$

$$\Delta_r G^0 = 2G_m{}^0(SO_3) - 2G_m{}^0(SO_2) - G_m{}^0(O_2)$$

$$\text{Or: } \Delta_r G^0 = 2\Delta_f G^0(SO_3) - 2\Delta_f G^0(SO_2) - \underset{0}{\underset{\uparrow}{\Delta_f G^0(O_2)}}$$

The standard Gibbs free energies of compounds and elements are given in tables (as functions of temperature).

Often in forms like this:

$$-\frac{G^0_{m,T} - H^0_{m,298}}{T}$$

standard molar enthalpy at 298 K

Or:

$$-\frac{G^0_{m,T} - H^0_{m,0}}{T}$$

standard molar enthalpy at 0 K (different from the usual convention), the enthalpy of a compound is taken equal to the enthalpy of formation ***at 0 K****.*

Advantage*: these quantities only slightly depend on temperature. It is easier to interpolate.*

2.8 Gibbs free energy of an ideal gas

Here we study the pressure dependence of the molar Gibbs free energy (at constant temperature).

The complete differential of the Gibbs free energy (for 1 mol substance):

$$dG_m = V_m dp - \cancel{S_m dT} \qquad (2.35)$$

*At **constant temperature** the second term can be neglected.*

V_m can be expressed from the ideal gas law:

$$V_m = \frac{RT}{p}$$

$$dG_m = RT\frac{dp}{p}$$

Integrate from the standard pressure p^0 to pressure p.

$$G_m - G_m^0 = RT(\ln p - \ln p^0) = RT\ln\frac{p}{p^0}$$

$$G_m(p,T) = G_m^0(T) + RT\ln\frac{p}{p^0} \qquad (2.37)$$

$$\Longrightarrow \quad \mu(p,T) = \mu^0(T) + RT\ln\frac{p}{p^0} \qquad (2.38)$$

The Gibbs free energy (chemical potential, (2.14)) increases with increasing pressure (the entropy decreases).

2.9 The chemical potential

It was introduced by Gibbs in 1875. It is denoted by μ *[Joule/mol]*

The word „potential" refers to physical analogies:

Masses fall from higher to lower gravitational potential.

Charges move from higher to lower electric potential.

The chemical substance moves from place where the chemical potential is higher to a place where it is lower (by diffusion).

Why do we need chemical potential? Is concentration not sufficient to describe the direction of transport of substances? Examples:

1. Two aqueous solutions of NaCl of different concentrations are layered on each other.

$$c_{NaCl}(1) > c_{NaCl}(2)$$

$$\mu_{NaCl}(1) > \mu_{NaCl}(2)$$

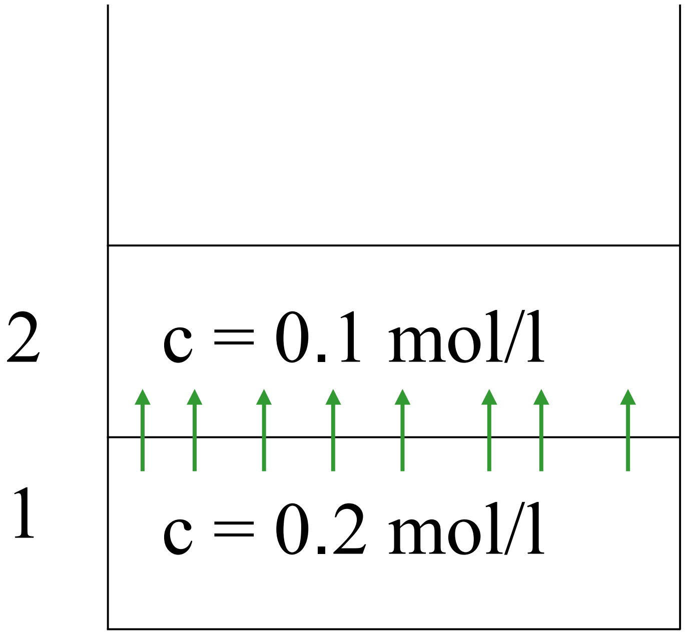


Fig. 2.11

The salt diffuses from the place where the concentration (and the chemical potential) is higher to the place where the concentration (and the chemical potential) is lower.

To explain this process we do not need μ.

2. There are two different solvents, water and CCl_4 . The solute is iodine. The concentration of iodine is higher in CCl_4 than in water

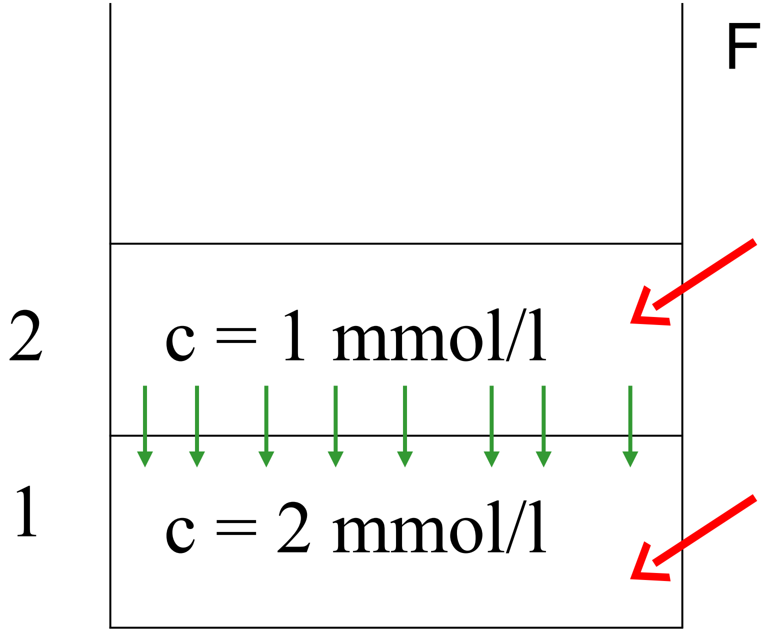


Fig. 2.12

2

c = 1 mmol/l

1

c = 2 mmol/l

Aqueous I_2 soln.

CCl_4 I_2 soln.

The iodine will diffuse from water to CCl_4 because its chemical potential is smaller in CCl_4 than in water (although its concentration is higher).

Extraction!!

Here we need μ.

$c_{iodine}(1) > c_{iodine}(2)$

$\mu_{iodine}(1) < \mu_{iodine}(2)$

The chemical potential is very important when we study solutions.

The chemical potential considers the effect of chemical environment

So far we have mainly dealt with ***closed systems*** *where the amount of substance does not change.*

The complete differentials of the four thermodynamic functions for closed systems if there is only pV work (no other work):

$dG = Vdp - SdT$ $\qquad G = G(T,p)$ (2.39a)

$dA = -pdV - SdT$ $\qquad A = A(T,V)$ (2.39b)

$dH = Vdp + TdS$ $\qquad H = H(p,S)$ (2.39c)

$dU = -pdV + TdS$ $\qquad U = U(V,S)$ (2.39d)

If the amount of substance also changes ***(open systems)****, the functions of state depend on* n_i*-s, too:*

$$G = G(T,p,n_1,n_2,\ldots)$$

$$A = A(T,V,n_1,n_2,\ldots)$$

$$H = H(p,S,n_1,n_2,\ldots)$$

$$U = U(V,S,n_1,n_2,\ldots)$$

The complete differentials include the amounts of substances, too. E.g.

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i \qquad (2.40)$$

$n_i = n_1, n_2, n_3$, etc. $\quad j \neq i$

The Σ has as many terms as the number of components.

E.g. for a two component system:

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1} dn_2 \qquad (2.41)$$

The derivatives with respect to the amounts of substance are called ***chemical potentials****.*

The chemical potential of the component ***i:***

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad j \neq i \qquad (2.42)$$

The chemical potential of a component is equal to the change of the Gibbs free energy of the system if one mol component is added to infinite amount of substance .

(Infinite so that the composition does not change.)

The complete differential of G in an open system:

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$

In short:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \qquad (2.43)$$

At constant temperature and pressure:

many components

$$dG_{p,T} = \sum_i \mu_i dn_i$$

two components

$$dG_{p,T} = \mu_1 dn_1 + \mu_2 dn_2 \quad (2.44a)$$

Integrating (with constant composition, p and T):

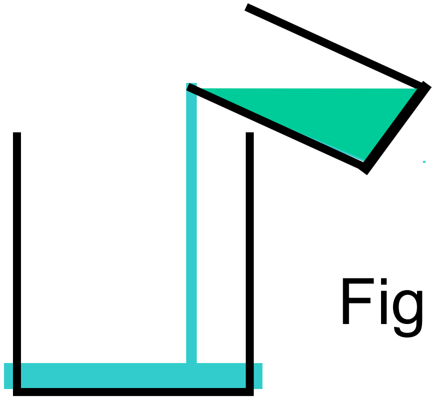


Fig. 2.13

$$G_{p,T} = \mu_1 n_1 + \mu_2 n_2$$

$$G_{p,T} = \sum_i \mu_i n_i \quad (2.44b)$$

The Gibbs free energy of the system can be calculated from the chemical potentials at constant p and T.

Molar Gibbs free energies of pure components

Watch out!

$$G \neq \sum G_{mi} \cdot n_i \qquad (2.45)$$

In solutions S, A and G are not additive.

$$Solvent \quad effect: G_{mi} \neq \mu_i$$

$$\left(\frac{G_i}{n_i}\right)_{p,T} \neq \left(\frac{\partial G}{\partial n_i}\right)_{n_j,p,T} \quad j = 1,2,..,k \quad j \neq i \qquad (2.46)$$

This equation (2.46) means the molar Gibbs free energy of the pure component i is not equal to its partial molar Gibbs free energy (chemical potential) in the same solution.

Relation between μ and Helmholtz free energy:

$A = G - pV$ *and* $dA = dG - pdV - Vdp$

substituting $dG = Vdp - SdT + \sum_i \mu_i dn_i$

$$dA = -pdV - SdT + \sum_i \mu_i dn_i \qquad (2.47)$$

At constant volume and temperature:

$$dA_{V,T} = \sum_i \mu_i dn_i \qquad (2.48)$$

Similarly, it can be proved like (2.42) for G

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} \qquad (2.49a)$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} \qquad (2.49b)$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} \qquad (2.49c)$$

$$H = G + TS \quad dH = dG + TdS + SdT$$

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$dH = Vdp + TdS + \sum_i \mu_i dn_i$$

At constant S and p:

$$dH_{S,p} = \sum_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S,p,n_j} \qquad (2.49b)$$

$$U = H - pV \quad dU = dH - pdV - Vdp$$

$$dH = Vdp + TdS + \sum_i \mu_i dn_i$$

$$dU = -pdV + TdS + \sum_i \mu_i dn_i$$

At constant S and V:

$$dU_{S,V} = \sum_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} \qquad (2.49c)$$

The chemical potential of one component (pure) substances (see also 2.42):

$$G = n \cdot G_m \qquad (2.50)$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T} = G_m \qquad (2.51)$$

The chemical potential of a ***pure substance*** *is equal to the molar Gibbs free energy.*

The chemical potential of an ideal gas:

$$G_m = G_m^0 + RT \ln \frac{p}{p^0} \qquad (2.52a) \qquad \mu = \mu^0 + RT \ln \frac{p}{p^0} \qquad (2.52b)$$

$$\mu = G_m \qquad (2.53a) \qquad \mu^0 = G_m^0 \qquad (2.53b)$$

Standard chemical potential = standard molar Gibbs free energy (the Gibbs free energy of 1 mol ideal gas at p^0 pressure and at the given temperature): see (2.53b).

2.10 Conditions for phase equilibria

Consider a multicomponent system with several phases.

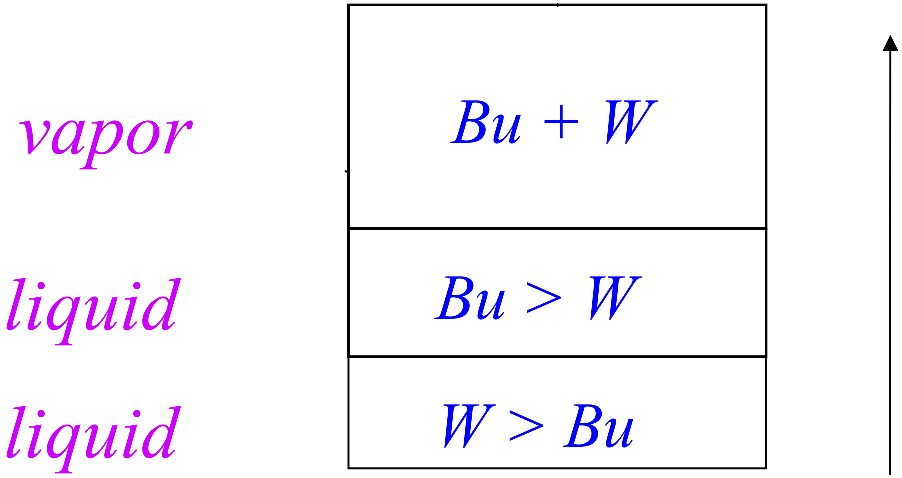
P*: number of phases*

C*: number of components.*

E.g.: butanol (Bu)-water (W) system

$$C = 2$$

$$P = 3$$



vapor $Bu + W$

liquid $Bu > W$

liquid $W > Bu$

Fig.2.14

In equilibrium the pressure and temperature are equal in all the phases.

$$dG_{p,T} = \sum \mu_i dn_i = 0$$ *i*=1,2,…,*C* (2.54a)

For C components and P phases:

$$dG_{p,T} = \sum_{j=1}^{P} \sum_{i=1}^{C} \mu_i^j dn_i^j = 0$$ (2,54b)

Suppose that dn_i mol of component i goes from phase j to phase k ($j \rightarrow k$) at constant pressure and temperature. (The amounts of all the other components remain unchanged.)

$$dn_i^k = dn_i \qquad dn_i^j = -dn_i$$

$$dG = dn_i^k \mu_i^k + dn_i^j \mu_i^j$$

$$dG = dn_i \mu_i^k - dn_i \mu_i^j$$

$$dG = dn_i \left(\mu_i^k - \mu_i^j \right) \qquad (2.55)$$

$$dG = dn_i\left(\mu_i^k - \mu_i^j\right)$$

1. In equilibrium *$dG = 0$, $dn_i \neq 0$, consequently:*

$$\mu_i^k = \mu_i^j \qquad (2.56)$$

*The chemical potential of component **i** is equal in the two selected phases.*

This equation is valid for any phases (P phases).

$$\mu_i^1 = \mu_i^2 = \ldots = \mu_i^j = \ldots \mu_i^P = \mu_i$$

In equilibrium the chemical potential of a component is equal in all the phases which are in contact (see also 2.23).

***2. No equilibrium**. Spontaneous process:*

$$dG_{p,T} < 0 \qquad (2.57)$$

$$dn_i\left(\mu_i^k - \mu_i^j\right) < 0 \qquad dn_i > 0 \qquad \mu_i^j > \mu_i^k$$

In a spontaneous process any component goes from the phase where its chemical potential is larger to the phase where its chemical potential is smaller.

Substance goes from phase j to phase k, consequence

2.11 The Gibbs' phase rule

The phase rule determines the number of intensive parameters that can be independently varied in equilibrium systems. This number depends on the number of phases and the number of components.

Phase: *a state of matter that is uniform throughout, not only in chemical composition but also in physical state.*

The number of Components: the minimum number of independent species necessary to define the composition of all the phases present in the system.

If there is no chemical reaction in the system the number of components is the number of different chemical substituents.

The degrees of Freedom (variance): is the number of intensive variables that can be changed independently without changing the number of phases.

The phase rule:

$$\boxed{F = C - P + 2} \tag{2.58}$$

Derivation: *pressure + temperature: 2, the rest (C-P) is the number of concentations varied independently.*

In case of P phases and C components:

C\P	A	B	C	.
1	c_1^A	c_1^B	c_1^C	.
2	c_2^A	c_2^B	c_2^C	.
3	c_3^A	c_3^B	c_3^C	.
.	.	.	.	.

$C \cdot P$ concentration data but not all of them are independent.

In each phase C-1 concentrations are sufficient. E.g. methane-ethane-propane gas mixture. If we know the mole fraction of the first two, the third one can be calculated:

$y_{pr} = 1 - (y_m + y_e)$ (y: mole fraction)

P phases: $\boxed{P(C-1)}$ *concentrations* (2.59)

In equilibrium the concentrations of a component in different phases are not independent (distribution in equilibrium):

$$\mu_1^A = \mu_1^B = \mu_1^C = \ldots \qquad \mu_2^A = \mu_2^B = \mu_2^C = \ldots$$ A,B,C phases

That means P-1 relationships for each component.

For C components $\boxed{C(P-1)}$ *has to be substracted from (2.59):*

$$\mathbf{F} = 2 + P(C-1) - C(P-1) = 2 + CP - P - CP + C = \mathbf{C-P+2} \qquad (2.60)$$

$\boxed{F = C - P + 2}$ or $F+P=C+2$

For one component systems (Fig. 2.15)

P	F
1	2 (T, p)
2	1 (T or p)
3	0 (triple point)

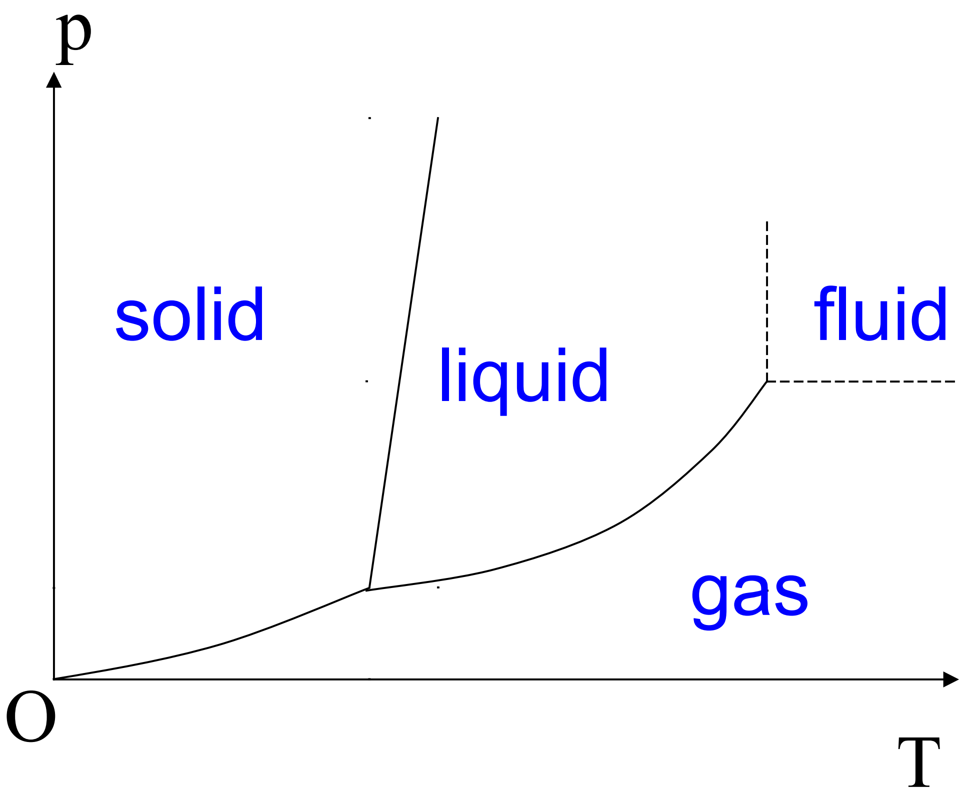


Fig. 2.15

$$\boxed{F = C - P + 2}$$

p-x,y phase diagram (p pure component, x, y mole fractions, liquid and gas, respectively)*

***Two component** systems*

P	F
1	3 (T, p, x_1)
2	2 of them
3	1 of them

For plotting in two dimensions one parameter has to be kept constant (p or t)

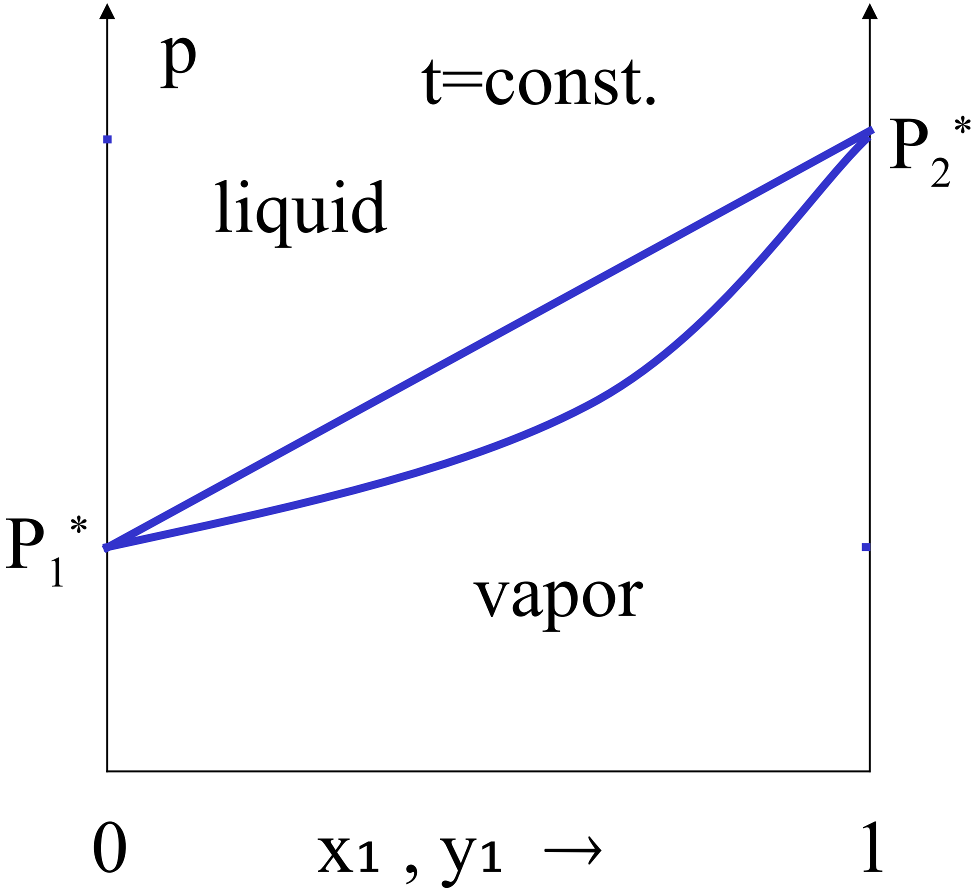


Fig. 2.16

The number of Components: the minimum number of independent species necessary to define the composition of all the phases present in the system.

E.g. the NaCl - water system. The number of the Na^+ and the Cl^- ions are not independent. Because of electroneutrality their numbers must be equal.

We will see latter that when the $NaCl = Na^+ + Cl^-$ reaction is in equilibrium than $\mu^{i}_{\mathrm{NaCl}} = \mu^{i}_{\mathrm{Na}^+} + \mu^{i}_{\mathrm{Cl}^-}$

As the concentration of ions are equal $\mu^{i}_{\mathrm{NaCl}} = \mu^{j}_{\mathrm{NaCl}} \Longleftrightarrow \begin{matrix} \mu^{i}_{\mathrm{Na}^+} = \mu^{j}_{\mathrm{Na}^+} \\ \mu^{i}_{\mathrm{Cl}^-} = \mu^{j}_{\mathrm{Cl}^-} \end{matrix}$

→ NaCl – water system has two components.

The number of Components: the minimum number of independent species necessary to define the composition of all the phases present in the system.

The $CaCO_3$,CaO, CO_2 system has two components, too.
Three chemical substances but one reaction between them:

$$CaCO_3 = CaO + CO_2 \quad \Longleftrightarrow \quad \mu^{i}_{CaCO_3} = \mu^{i}_{CaCO} + \mu^{i}_{CO_2}$$

⟹ $CaCO_3$,CaO, CO_2 system has two components.

2.12 Equation of state for real gases

Ideal gas, see subsection 1.4 :

1. No interaction between molecules
(the potential energy of interaction is 0).

2. The molecules are mass points.

*We study in this subsection the **real gas equations**: the van der Waals and the virial equations of state.*

*The potential energy between two molecules as the function of distance **r** (see also the similar figure 1.11)*

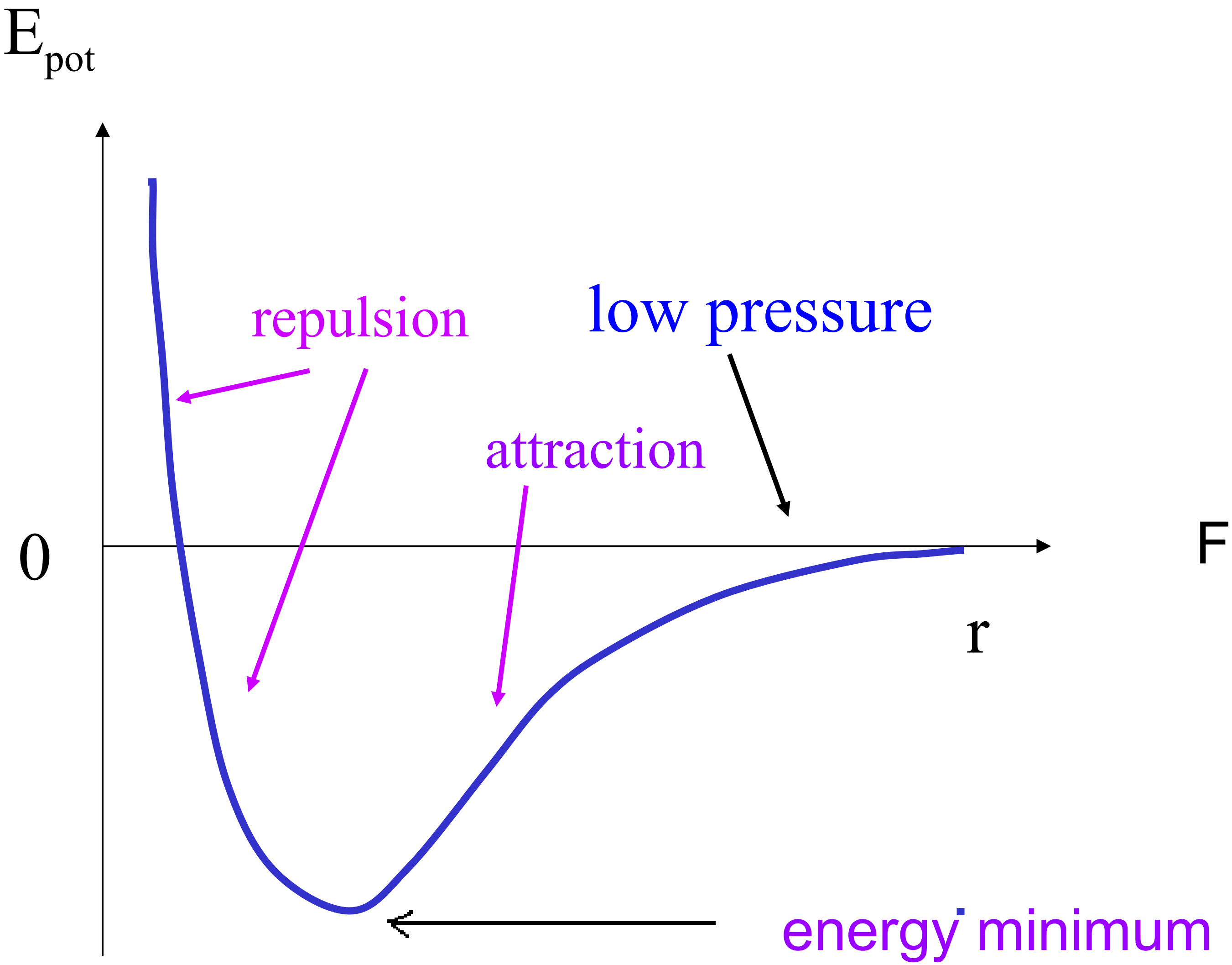


Fig. 2.17

The van der Waals equation of state

Van der Waals modified the ideal gas law with two constants in order to include the molecules' own sizes and the (attractive) interactions.

Ideal gas: $$p = \frac{RT}{V_m}$$

Becauese of the size of the molecules the volume available for motion is smaller: negative correction of V_m .

$$p = \frac{RT}{V_m - b} \qquad (2.61a)$$

Because of attractive forces molecule pairs are formed temporarily (decreasing the pressure). If it is an equilibrium reaction:

$$(M+M=M_2) \longrightarrow [M_2]=K\cdot[M]^2 \qquad (2.61b)$$

The decrease of pressure is proportional to the concentration. The concentration is the reciprocal of the molar volume. Summarizing the 2.61 equations ($V_m = V/n$):

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Rearranging we have the van der Waals equation

$$\left(p + \frac{a}{V_m^2}\right)\cdot(V_m - b) = RT \qquad (2.62)$$

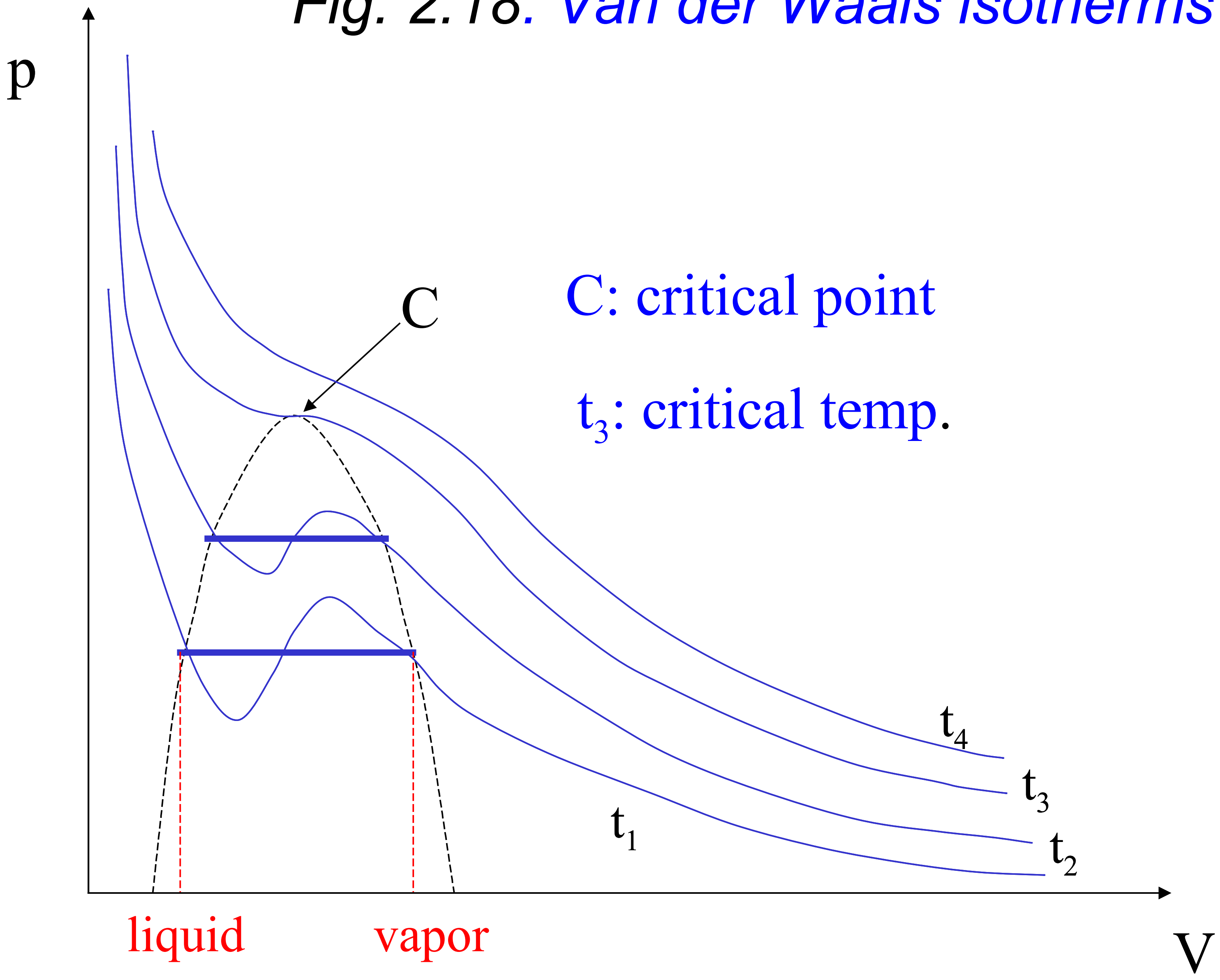
Other forms of the van der Waals equation:

$$\left(p + \frac{a \cdot n^2}{V^2} \right) \cdot \left(\frac{V}{n} - b \right) = R \cdot T \qquad (2.63a)$$

$$\left(p + \frac{a \cdot n^2}{V^2} \right) \cdot (V - n \cdot b) = n \cdot R \cdot T \qquad (2.63b)$$

The van der Waals equation is cubic for V. That means, in a certain range three different volumes belong to one pressure. – These parts of the isotherms have no physical reality, see Fig. 2.18.

Fig. 2.18: Van der Waals isotherms



C: critical point

t$_3$: critical temp.

Advantage of the van der Waals equation: it has two constants only. It is simple in comparison of a lot of other types of real gas equations.

Disadvantage: it is not accurate enough.

Virial equation of state

$$\frac{pV_m}{RT} = 1 + \frac{\overset{\text{second}}{B(T)}}{V_m} + \frac{\overset{\text{third}}{C(T)}}{V_m^2} + \frac{\overset{\text{fourth}}{D(T)}}{V_m^3} + \dots \qquad (2.64)$$

virial coefficient

This virial equation of state it is basically a power series of the concentration ($1/V_m$) Substituting V/n for V_m:

$$\frac{pV}{nRT} = 1 + \frac{n \cdot B(T)}{V} + \frac{n^2 \cdot C(T)}{V^2} + \frac{n^3 \cdot D(T)}{V^3} + \dots$$

(2.65)

2.13 The principle of corresponding states

The deviation from the ideal gas law can be expressed with the **compressibility factor**:

$$z = \frac{pV_m}{RT} \tag{2.66}$$

$z = 1$ → ideal gas

$z > 1$ → less compressible - repulsive forces dominate.
(high pressures, high temperatures)

$z < 1$ → more compressible - attractive forces dominate.
(intermediate pressures, low temperatures)

$$z = z(p, T, \text{material}) \qquad (2.67)$$

The behaviour of real gases is found very similar if their properties are studied as functions of reduced pressure (the pressure divided by the critical pressure) and reduced temperature (the temperature divided by the critical temperature).

$$\pi = \frac{p}{p_C} \qquad \vartheta = \frac{T}{T_C} \qquad \varphi = \frac{V_m}{V_C} \qquad (2.68)$$

reduced pressure *reduced temperature* *reduced volume*

***Law of corresponding states**: if two reduced parameters of two different gases are equal then the third ones are equal, too.*

That means if $\pi_A = \pi_B$ *and* $\vartheta_A = \vartheta_B$ *then* $\varphi_A = \varphi_B$

In this case the two gases are in "corresponding state". Their compressibility factors are nearly the same.

If the reduced pressures and reduced temperatures of two gases are the same (i.e. they are in corresponding state) then their compressibility factors are the same, too.

Therefore if $\pi_A = \pi_B$ *and* $\vartheta_A = \vartheta_B$ *then* $z_A = z_B$

This is not a strict law, rather an empirical rule for practical use.

We can plot a general reduced compressibility diagram valid for all the gases (see Figs. 2.19a anb).

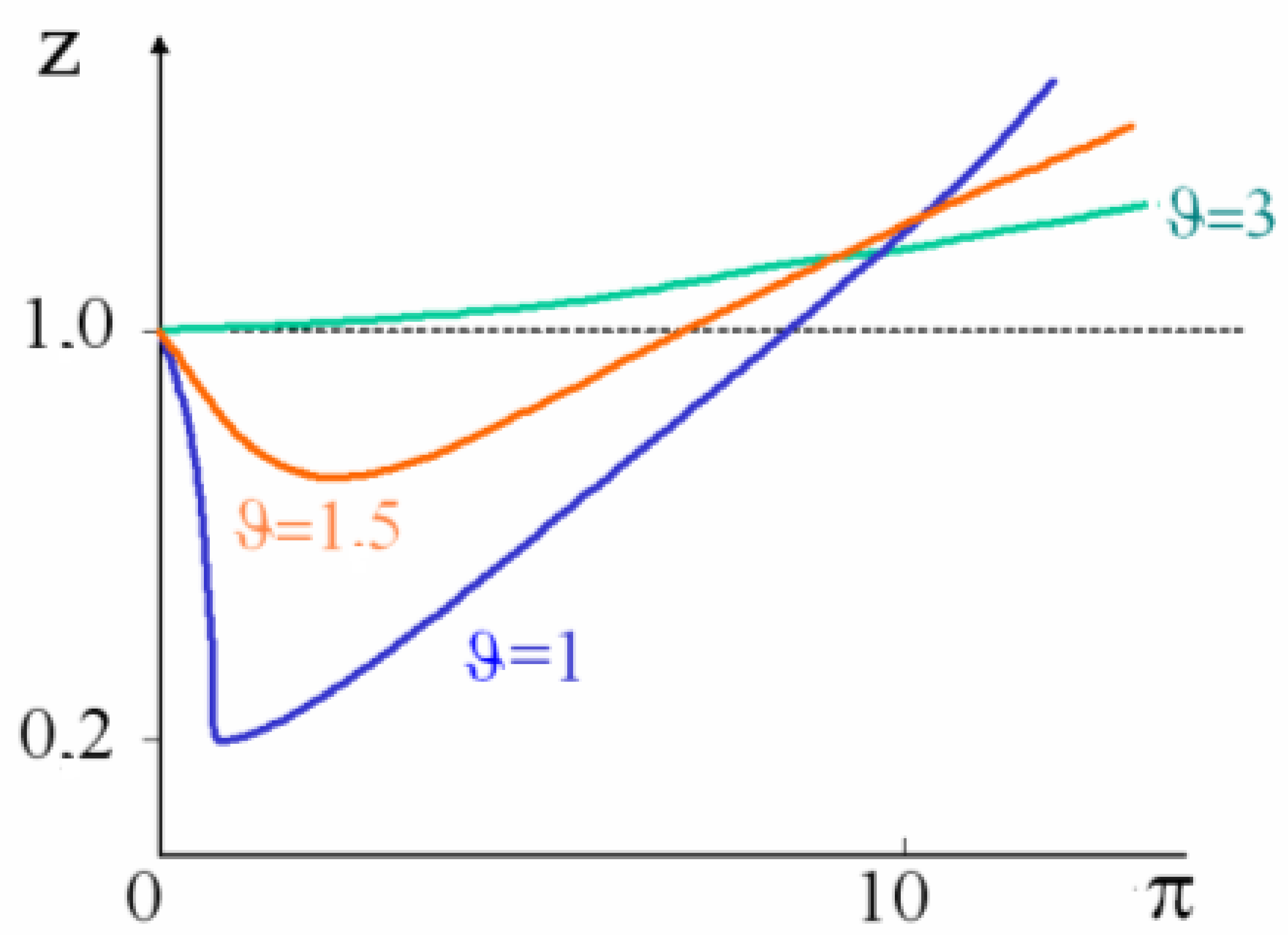


Fig. 2.19a

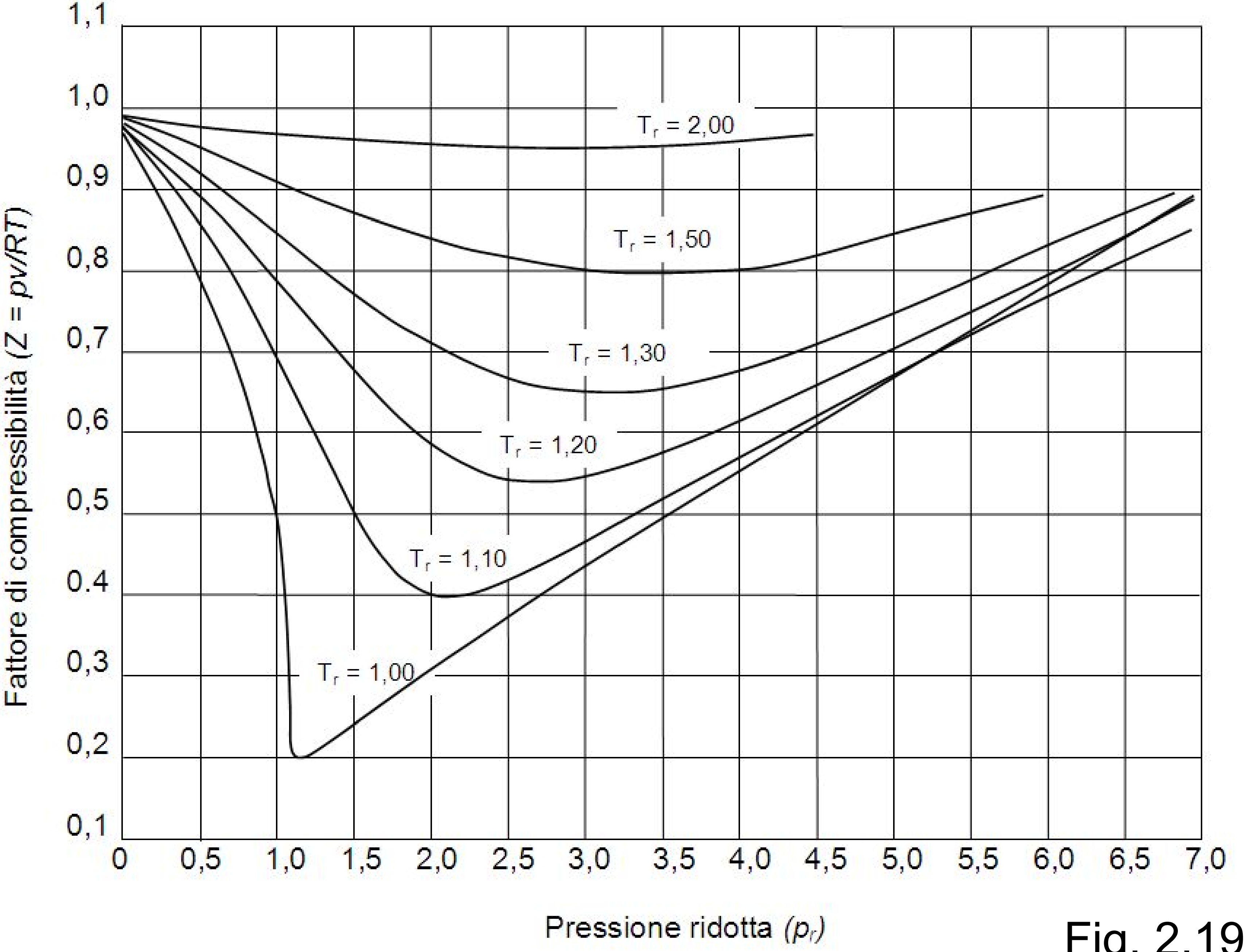

1,1
1,0
0,9
0,8
0,7
0,6
0,5
0.4
0,3
0,2
0,1
Fattore di compressibilità (Z = pv/RT)
0
0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0
5,5
6,0
6,5
7,0
Pressione ridotta (p_r)
T_r = 2,00
T_r = 1,50
T_r = 1,30
T_r = 1,20
T_r = 1,10
T_r = 1,00

Fig. 2.19b

Near π=0 each curve approaches z=1 (ideal gas).

There exist two types of problems:

A) *p and T are known and* ***V**$_m$* *has to be determined.*

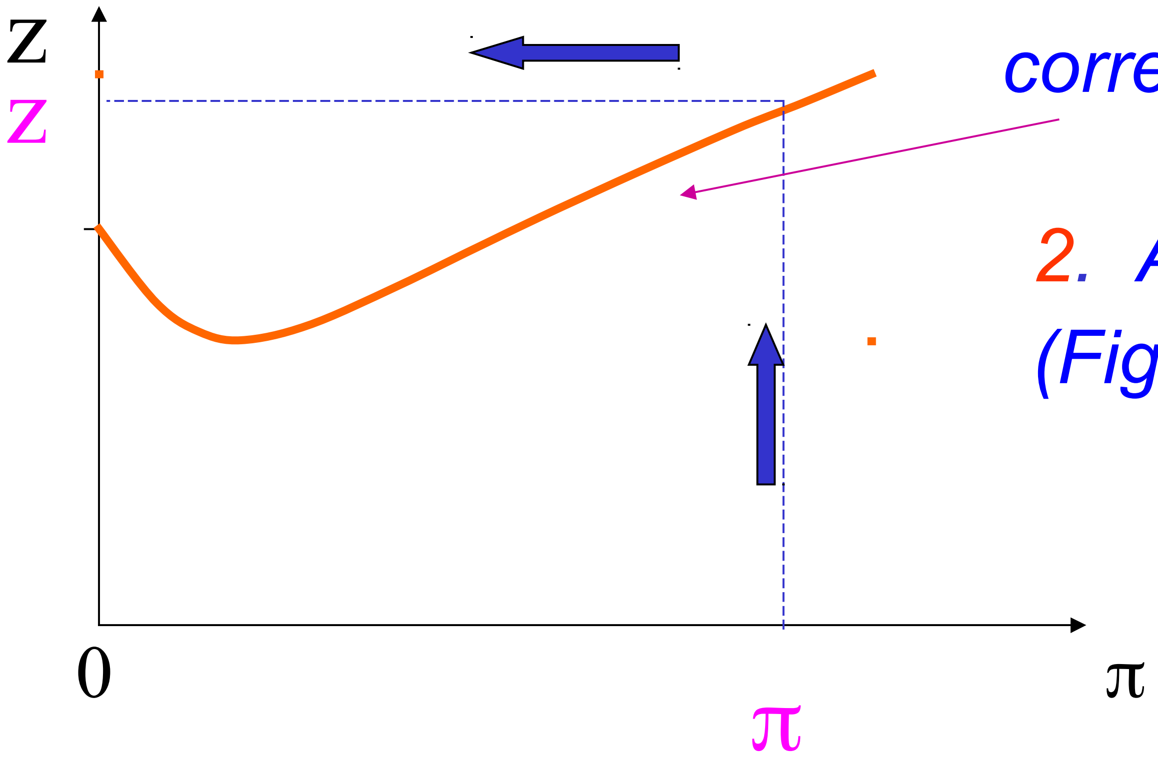


Fig. 2.20

1. *$\vartheta = T/T_C$, we select the corresponding isotherm.*

2. *At $\pi = p/p_C$ we read z (Fig. 2.20)*

3. $$V_m = \frac{zRT}{p} \quad (2.69)$$

*B) V_m and T are known, **p** has to be determined.*

Both p and z are unknown. Applying the definition of π (2.68)

$$z = \frac{pV_m}{RT} = \frac{p_C V_m}{RT} \cdot \pi \qquad (2.70)$$

Linear equation, slope (Fig. 2.21) z/π

$$\tan\alpha = \frac{p_C V_m}{RT}$$

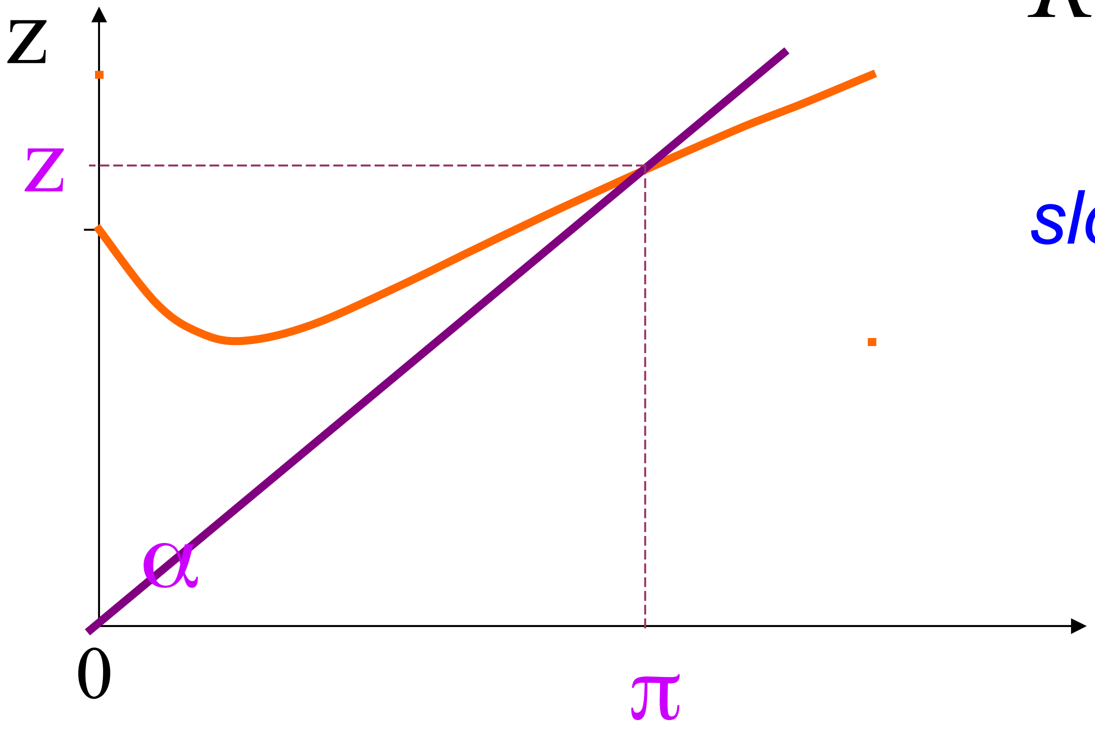


Fig. 2.21

Where the straight line crosses the corresponding isotherm, we can read both z and π, since

$$p = p_C \cdot \pi \quad or$$

$$p = \frac{zRT}{V_m}$$

2.14 The Joule-Thomson effect

In industry it is frequently applied the expansion of gases through throttles.

For example, in chemical works high pressure steam network are used often. On the site of application the reduced pressure is needed.

If high pressure gases are expanded adiabatically through a throttle, the temperature usually changes. Most frequently the temperature drops. (This is the basis of liquefying gases.)

Production of dry ice in a lab.

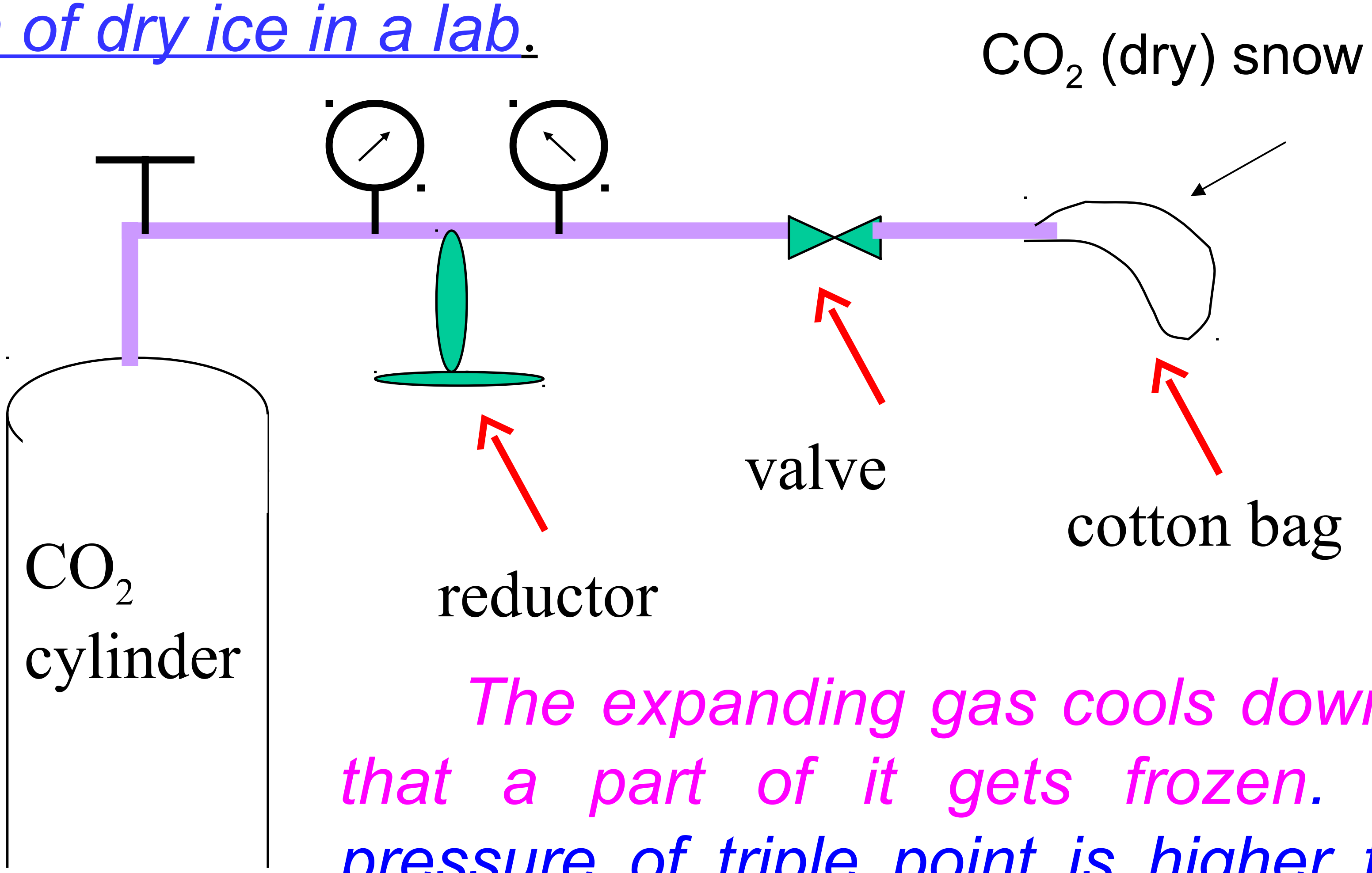
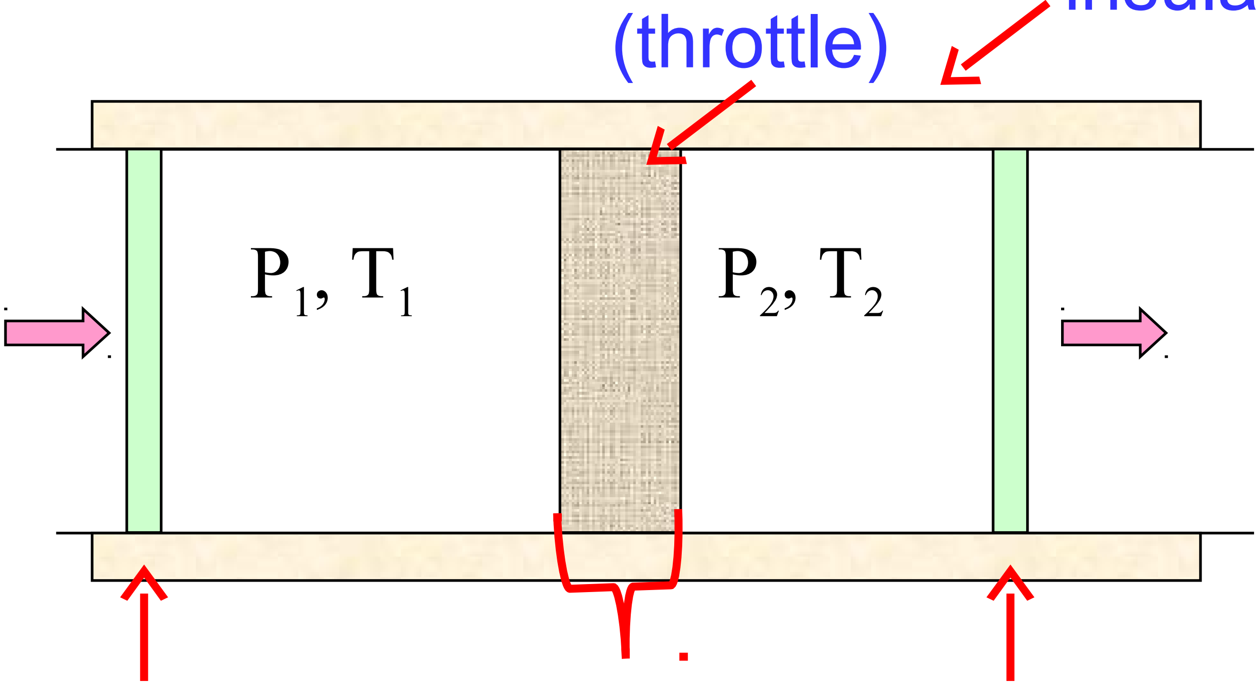


Fig. 2.22

The expanding gas cools down so that a part of it gets frozen. The pressure of triple point is higher than atmospheric pressure, therefore CO_2 *does not exist in liquid state on atmospheric pressure (see subsection 2.14)*

The experiment of Joule and Thomson



porous plug (throttle)

insulation

P_1, T_1

P_2, T_2

piston

system

piston

Fig. 2.23

A) We apply the first law for the ***throttle*** *as an open system (subsection 1.12)*

$$\Delta U = Q + W + H_{in} - H_{out} \qquad (1.52)$$

Steady state: $\Delta U = 0$ *Adiabatic:* $Q = 0$

No work done in the throttle: $W = 0$ $\Rightarrow$ $\boxed{\Delta H = 0}$

B) We apply the first law for the ***whole system*** *including the cylinders, the gas and the pistons. This is regarded as a closed system (follow Fig. 2.23).*

$$\Delta U = W + Q \qquad \textit{Adiabatic: } Q = 0$$

Initial state (state 1), all the gas is in the left hand side

Final state (state 2), all the gas is in the right hand side

Therefore $\Delta U = W$

and the work is $U_2 - U_1 = p_1V_1 - p_2V_2$ (2.71)

Namely, in the left hand side work is done ***on*** *the system, in the right hand side work is done* ***by*** *the system.*

$$U_2 + p_2V_2 = U_1 + p_1V_1 \quad \text{i.e.} \quad H_2 = H_1 \Rightarrow \boxed{\Delta H = 0}$$

Therefore if a gas gets through a throttle adiabatically, its enthalpy does not change.

How does the temperature change?

In case of an ***ideal gas*** *T does not change. (Enthalpy depends on T only, if H does not change, T does not change either).*

For **real gas:** We define the Joule-Thomson coefficient:

$$\lim_{\Delta p \rightarrow 0}\left(\frac{\Delta T}{\Delta p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_H \qquad (2.72)$$

μ_{JT} can be positive, zero and negative

μ_{JT} >0: the gas cools down (dp is always negatíve)

μ_{JT} <0: the gas warms up

μ_{JT}=0: the temperature does not change

This is possible since there are certain temperatures and pressures for real gases, too, where we cannot find a temperature change when performing the Joule-Thomson experiment.

This statements can clearly understandable on a p-T diagram (Fig. 2.24).

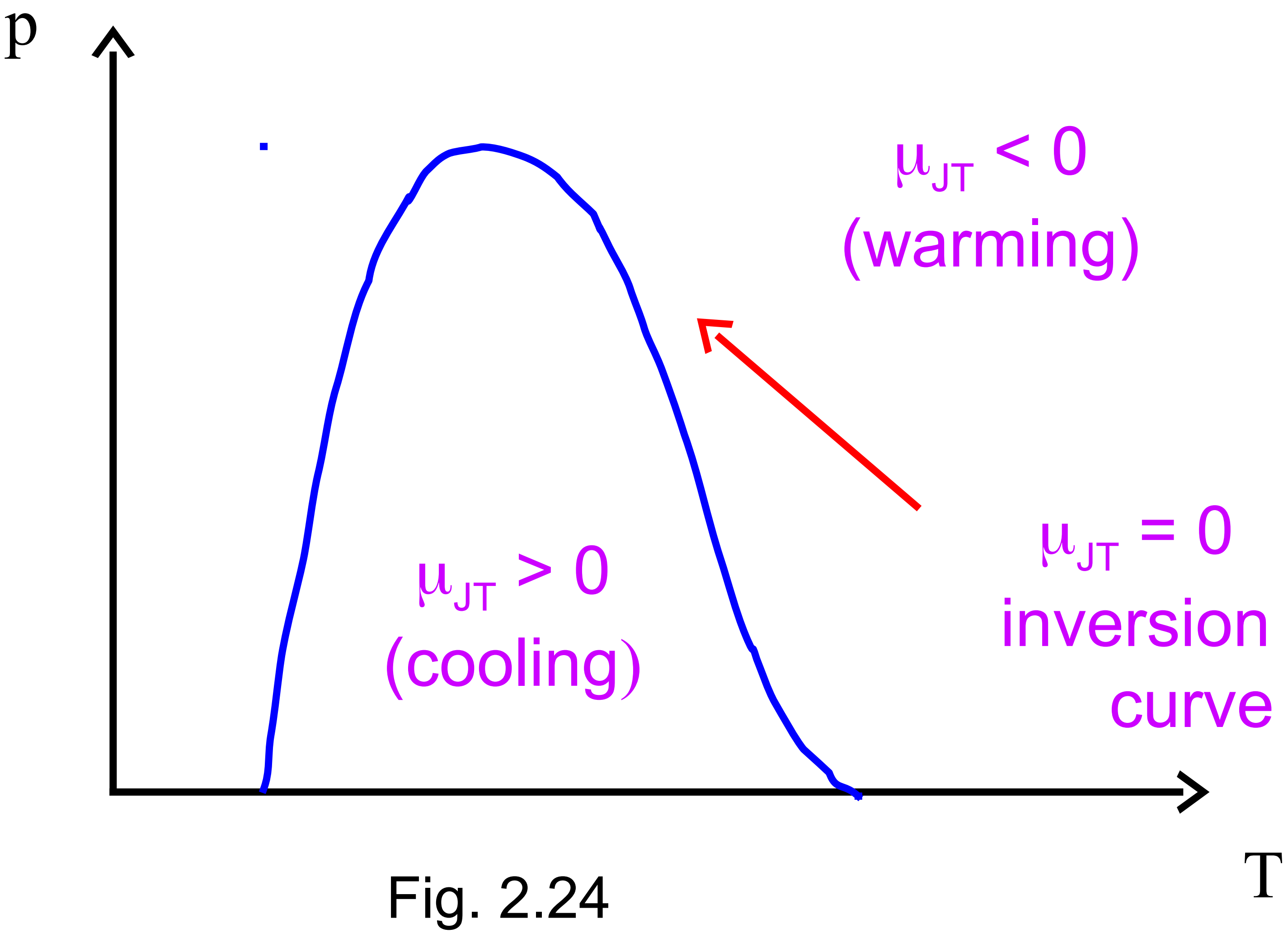


Fig. 2.24