

# F4280 Technologie depozice tenkých vrstev a povrchových úprav

## 2. Gas Kinetics

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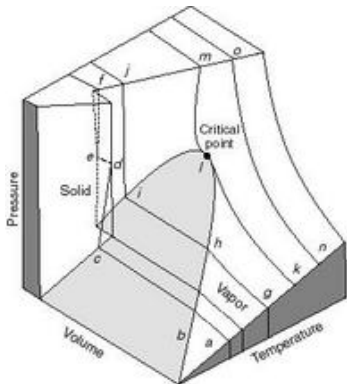


## Outline - chapter 2. Gas Kinetics

- 2.1 Vapors and Gases
- 2.2 Maxwell-Boltzmann Distribution
- 2.3 Ideal-Gas Law
- 2.4 Molecular Impingement Flux
- 2.5 Units of Measurement
- 2.6 Knudsen Equation
- 2.7 Mean Free Path
- 2.8 Transport Properties

# p-V-T diagram

The possible equilibrium states can be represented in **pressure-volume-temperature (p-V-T) space** for fixed amount of material (e.g. 1 mol =  $6.02 \times 10^{23}$ ):



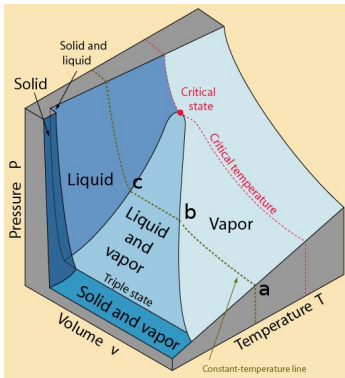
A cut through the p-V-T surface below critical point for fixed  $T \Rightarrow$  relationship between  $p$  and  $V_m$  (molar volume)

- ▶ point a: highest  $V$  (lowest  $p$ ) - vapor phase
- ▶ from point a to b: reducing  $V \rightarrow$  increasing  $p$
- ▶ point b: condensation begins
- ▶ from point b to c:  $V$  is decreasing at fixed  $p$  and  $T$  ( $b - c$  line is  $\perp$  to the p-T plane,  $p$  is called **saturation vapor pressure**  $p_v$  or just **vapor pressure**)
- ▶ point c: condensation completed

If  $V$  is abruptly decreased in  $b - c$  transition  $p$  would be pushed above the line  $b - c \Rightarrow$  **non-equilibrium supersaturated vapors**

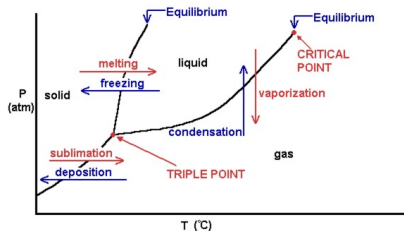
# p-V-T diagram

It is important to distinguish between the behaviors of **vapors** and **gases**:

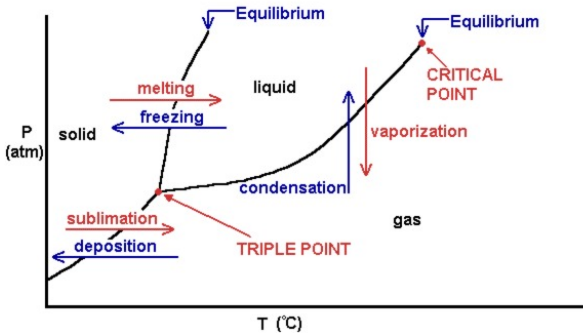


- ▶ **vapors**: can be condensed to liquid or solid by compression at fixed  $T \Rightarrow$  below **critical point** defined by  $p_c$ ,  $V_c$  and  $T_c$
- ▶ **gases**: monotonical decrease of  $V$  upon compression  $\Rightarrow$  no distinction between the two phases

Surfaces “liquid-vapor”, “solid-vapor” and “solid-liquid” are perpendicular to the p-T plane  $\Rightarrow$  their projection on that plane are lines.



# p-T diagram



- ▶ **triple point:** from triple line  $\perp$  to p-T plane
- ▶ below  $T$  of triple point: liquid-phase region vanishes  $\Rightarrow$  condensation directly to the solid phase, vaporization in this region is **sublimation**
- ▶ pressure along borders of vapor region is **vapor pressure**  $p_v$
- ▶  $p_v$  increases exponentially with  $T$  up to  $p_c$  that is well above 1 atm  $\Rightarrow$  deposition of thin films is performed at  $p \ll p_c$ , either  $p > p_v$  (supersaturated vapors) or  $p < p_v$

# Maxwell-Boltzmann Distribution

Distribution of random velocities  $\vec{V}$  in equilibrium state

$$f(\vec{V}) = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{mV^2}{2k_B T} \right) \quad (1)$$

where  $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$  (or  $\text{J K}^{-1}$ ) is the Boltzmann constant,  $n$ ,  $T$  and  $m$  are particle density, temperature and mass, respectively.

**If the drift velocity is zero** we do not need to distinguish between the velocity and random velocity, i.e.  $\vec{v} \equiv \vec{V}$ .

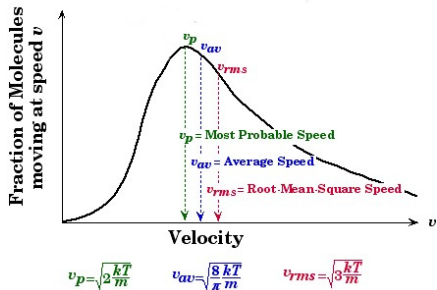
**Maxwell-Boltzmann distribution is isotropic**  $\Rightarrow F(v)$  distribution of speeds  $v \equiv |\vec{v}|$  can be defined by integration of  $f(v)$  in spherical coordinates

$$F(v)dv = \int_0^\pi \int_0^{2\pi} f(v)v^2 \sin\theta d\phi d\theta dv \quad (2)$$

resulting in

$$F(v) = 4\pi v^2 n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{mv^2}{k_B T} \right) \quad (3)$$

# Mean (Average) Speed, Molecular Impingement Flux



**Mean speed:**

$$\langle v \rangle = v_{av} = \frac{1}{n} \int_0^{\infty} F(v) v dv = \sqrt{\frac{8k_B T}{\pi m}} \quad (4)$$

or

$$v_{av} = \sqrt{\frac{8RT}{M}} \quad (5)$$

using **molar mass**  $M = mN_A$  in kg/mol and **gas constant**

$$R = k_B N_A = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

where  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$  is Avogadro's number

**Root-mean-square (rms) speed:**

$$v_{rms} = \frac{1}{n} \int_0^{\infty} F(v) v^2 dv = \sqrt{\frac{3k_B T}{\pi m}} \quad (6)$$

The **most probable speed**  $v_p$ :

$$\left( \frac{dF(v)}{dv} \right)_{v=v_p} = 0 \Rightarrow v_p = \sqrt{\frac{2k_B T}{m}} \quad (7)$$

## Ideal-Gas Law

From the definition of pressure for ideal gas (not necessary to consider pressure tensor but only scalar pressure)

$$p = \frac{1}{3} mn \langle \vec{v}_x^2 + v_y^2 + v_z^2 \rangle = \frac{1}{3} mn \langle \vec{v}^2 \rangle = m \int_V v^2 f(v) d^3 v. \quad (8)$$

The ideal-gas law is obtained by integration of (8) using Maxwell-Boltzmann distribution:

$$p = nk_B T \quad \text{or} \quad \frac{pV}{T} = Nk_B \quad (9)$$

where  $N$  is the number of particles.

Chemists are used to work in molar amounts:

- ▶ molar concentration  $n_m = n/N_A \Rightarrow p = n_m RT$
- ▶ number of moles  $N_m = N/N_A \Rightarrow p = N_m RT/V$
- ▶ molar volume  $V_m = V/N_A \Rightarrow p = RT/V_m$

The **ideal gas is obeyed if**

- ▶ the volume of molecules in the gas is much smaller than the volume of the gas
- ▶ the cohesive forces between the molecules can be neglected.

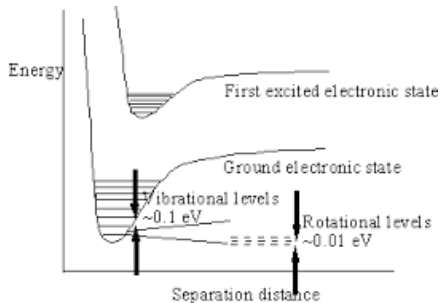
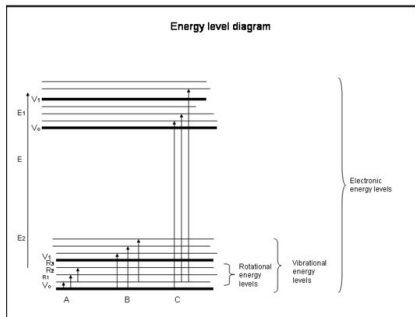
Both assumptions are fulfilled for low  $n \Rightarrow$  always fulfilled for thin film deposition from the vapor phase ( $T > T_{\text{room}}$  and  $p \leq p_{\text{atm}}$ ), i.e. well away from the critical point (most materials  $p_c \gg 1 \text{ atm}$  or if not  $T_c \ll 25 \text{ }^\circ\text{C}$ )



# Energy Forms Stored by Molecules

Molecules can store energy in various forms. Their energetic states are quantized (spacing between energy levels  $\Delta E$ )

- ▶ electronic excitations -  $\Delta E_e$  is highest, transitions between different electronic states are possible only for extremely high  $T$  or collision with energetic particle
- ▶ vibrational excitations - energy levels correspond to different vibration modes of the molecule,  $\Delta E_v \approx 0.1$  eV (1 eV = 11 600 K)
- ▶ rotational excitations - different rotational modes of the molecule,  $\Delta E_r \approx 0.01$  eV
- ▶ translational energy - above performed description of molecular random motion  $E_t = 1/2mV^2$ , no details of inner molecule structure are considered,  $\Delta E_t$  negligible at ordinary  $T$ .



## Energy Content of Gas

From definition of absolute temperature - the mean thermal energy  $kT/2$  belongs to each translational degree of freedom and molecular translation energy is

$$E_t = \frac{3}{2} k_B T \quad (10)$$

⇒ **equipartition theorem of classical statistical mechanics**. Classical statistical treatment assumes very close quantized energy levels of molecules, i.e. **approximated as a continuum**. It is a good assumption for **translational** energy when  $T \gg 0$  K.

- ▶ For **atomic** gases,  $E_t$  is total kinetic energy content.
- ▶ For **molecular** gases,  $E_r$  is added at ordinary  $T$  and  $E_v$  at very high  $T$ :

**Molar heat capacity at constant volume**  $c_V$  (for molecular gas) [J/(mol.K)] - increase of total kinetic energy for increasing  $T$ :

$$\frac{c_V}{N_A} = \frac{dE_m}{dT} = \frac{d(E_t + E_r + E_v)}{dT} \quad (11)$$

for atomic gases

$$c_V = \frac{3}{2} R = \frac{3}{2} k N_A$$

for small diatomic molecules at room  $T$

$$c_V = \frac{5}{2} R$$

- two rotational degrees of freedom are excited but vibrational ones are not

## Energy Content of Gas

The heat capacity of any gas is larger when measured at constant pressure  $c_p$  - heat input is doing  $p dV$  work on the surroundings in addition to adding kinetic energy to the molecules:

$$c_p = c_v + R \quad (12)$$

We can write from thermodynamics

$$c_v = \left( \frac{\partial U_m}{\partial T} \right)_v \quad (13)$$

where  $U_m$  is internal energy per mol  $U_m = E_m N_A$  and

$$c_p = \left( \frac{\partial H_m}{\partial T} \right)_p \quad (14)$$

where  $H_m$  is enthalpy per mol  $H_m = U_m + pV_m \Rightarrow$

$$\left( \frac{\partial H_m}{\partial T} \right)_p = \left( \frac{\partial U_m}{\partial T} \right)_p + p \left( \frac{\partial V_m}{\partial T} \right)_p \quad (15)$$

giving  $c_p = c_v + R$

## Molecular Impingement Flux - Knudsen Equation

The **molecular impingement flux** at a surface is a fundamental determinant of film deposition rate:

$$\Gamma = n \langle v \cos \theta \rangle = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} f(v) v^2 \cos \theta \sin \theta d\phi d\theta dv \quad (16)$$

Substituting Maxwell-Boltzmann distribution

$$\Gamma = n \left( \frac{k_B T}{2\pi m} \right)^{1/2} = \frac{1}{4} n v_{av} \quad (17)$$

## 2.5 Units of Measurement

see Smith's book

## 2.6 Knudsen Equation

see Smith's book

## 2.7 Mean Free Path

see Smith's book

## 2.8 Transport Properties

see Smith's book