Syllabus

1. Introduction

2. Fluids

1. General Characteristics
2. Dispersions
3. **Thermodynamics**
4. Transport Phenomena
5. Solutions
6. Surface Tension
7. Electrical Properties
8. Optical Properties
9. Biological Fluids

Physics of Microfluidic Systems

1. Navier-Stokes Equation
2. Laminar and Turbulent Flow
3. Fluid Dynamics
4. Fluid Networks
5. Transport of Heat
6. Interfacial Surface Tension
7. Electrokinetics

2.3.1. Heat and Temperature

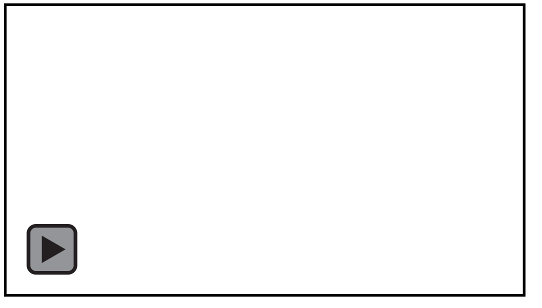
- Thermal energy per molecule

$$E_N = \frac{f}{2} k_\mathrm{B} T$$

  - In thermal equilibrium
  - Number of degrees of freedom (DoFs) f
  - Boltzmann constant $k_\mathrm{B} = 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
  - Heating 1 mol of ideal gas by $1\ \mathrm{K}$ consumes $4.16\ \mathrm{J}$ per DoF

- Three translational DoFs: $f = 3$

$$\bar{E}_\mathrm{kin} = \frac{3}{2} k_\mathrm{B} T$$



  - Also, rotational and vibrational DoFs f in (multi-atom) molecules

2.3.1 Zeroth Law of Thermodynamics

If two systems are both in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

2.3.1. Heat and Temperature

- Mean kinetic energy

$$\bar{E}_{\text{kin}} = \frac{1}{2} m \bar{v^2}$$

$$\bar{E}_{\text{kin}} = \frac{3}{2} k_{\text{B}} T$$

- Comparison: Mean (random, thermal) velocity

$$v_T = \sqrt{\bar{v^2}} = \sqrt{\frac{3 k_{\text{B}} T}{m}}$$

gas	$v_T / \text{m s}^{-1}$
hydrogen H_2	1839
nitrogen N_2	439
chlorine Cl_2	310

Table 2.1. Mean molecular velocities v_T for gases at $\theta = 0^\circ\text{C}$

2.3. Thermodynamics

1. Heat and Temperature
2. **Heat Capacity**
3. Chemical Potentials
4. Kinetic Theory of Gases
5. Compressibility
6. Thermal Expansion
7. Real Gases
8. Vapor Pressure

2.3.2. Heat Capacity

- Raising temperature of N particles by ΔT takes energy

$$\Delta E = N\frac{f}{2}k_\mathrm{B}\Delta T$$

$$E_N = \frac{f}{2}k_\mathrm{B}T$$

(per particle)

- Heat capacity

$$C = \frac{\Delta E}{\Delta T} = N\frac{f}{2}k_\mathrm{B}$$

- Specific heat capacity (for object)

$$C_m = \frac{C}{m} = \frac{\Delta E}{m\Delta T} = \frac{f}{2M}k_\mathrm{B}$$

- Molar heat capacity (for substance)

$$C_n = \frac{C}{n} = N_\mathrm{A}\frac{f}{2}k_\mathrm{B}$$

2.3. Thermodynamics

1. Heat and Temperature
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2.3.3. Internal Energy

- Internal energy U

$$\Delta U = U_B - U_A$$

  - State property
  - No absolute value, only difference / changes matter

- First Law of Thermodynamics: Equivalence of Energies
  - Mechanical W and Thermal Q: $4.18\ \mathrm{J} = 1\ \mathrm{cal}$
  - 1842: Robert Mayer and J. P. Joule

- Conservation of energy

$$\Delta U = Q - W$$

  - Amount of transferred heat Q
    - $Q > 0$: heat absorbed by system
  - (Expansion) work $W = p \cdot \Delta V$
    - $W > 0$: system delivers work, i.e., spends energy

2.3.3. Enthalpy

- Enthalpy (state property)

$$H = U + pV$$

  - Chemical reactions normally at constant pressure p

- **Heat** energy absorbed or released by system at $p = \mathrm{const.}$

$$Q_p = \Delta H = H_B - H_A = \Delta U + p\Delta V$$

  - Transferred heat Q_p= change in enthalpy
  - No volumetric expansion
    - Transferred heat = change in internal energy

- Example:

$$\mathrm{O_2(g)} \mapsto \mathrm{2O(g)} \;\; \Delta H_n = 495.3\,\mathrm{kJ\,mol^{-1}}$$

2.3.3. Entropy

- Entropy

$$S = k_B \ln W_{\text{prob}}$$

  - Probability W_{prob} of finding system in given state

- Entropy of „universe“

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{env}}$$

  - Entropy of environment S_{env}
  - Entropy of system under investigation S
  - S_{tot} constantly grows

$$\Delta S_{\text{env}} = -\frac{\Delta H}{T}$$

2.3.3. Gibbs Free Enthalpy

- Processes at constant T and p
  - Typical for chemical reactions
- Can process occur spontaneously?
  - Gibbs free enthalpy $G = H - TS$

$$\Delta G = \Delta H - T\Delta S = -T\Delta S_{\mathrm{tot}}$$

- $\Delta G < 0$ required for spontaneous process
  - Decrease in enthalpy H
  - Increase in entropy S
  - High temperature T

2.3. Thermodynamics

1. Heat and Temperature
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4. **Kinetic Theory of Gases**
5. Compressibility
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2.3.4. Kinetic Theory of Gases

- Pressure

$$p = \frac{F_\perp}{A}$$

  - Force perpendicular to surface A
  - Scalar
  - Isotropic

- Units
  - $1\ \text{Pa} = 1\ \text{N m}^{-2}$
  - 1 mbar = 1 hPa
  - 1 Torr (= mm Hg) = 133.4 Pa
  - 1 psi = 6897 Pa

- Standard pressure
  - 1 atm = 1 bar ≈ 1013 hPa =
  - 1013 mbar = 760 Torr = 14.7 psi

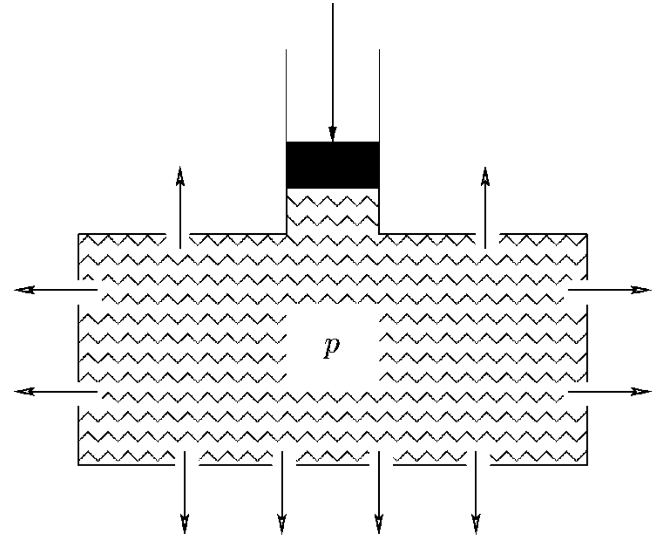


Fig. 2.1. Isotropy of pressure. A force $\boldsymbol{F}$ acting on the surface area A of the entrance of a vessel exerts a pressure $p = \boldsymbol{F}/A$ on the liquid. Neglecting gravitational force, this pressure p is uniformly distributed within the vessel and constant at all orifices

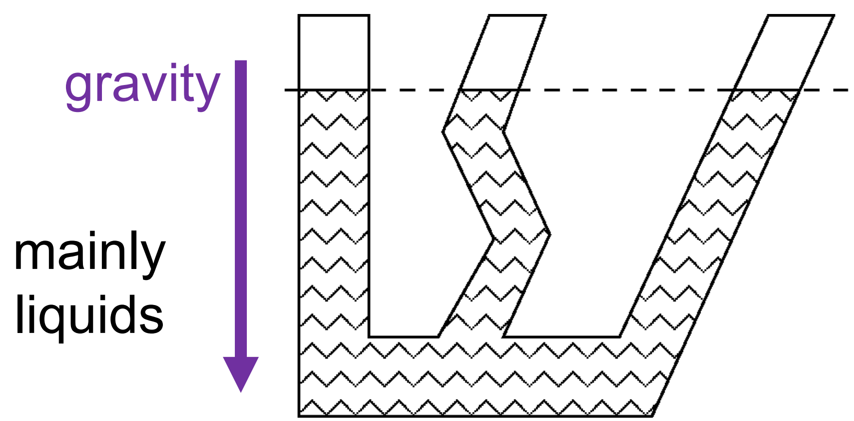


Fig. 2.2. Principle of interconnected tanks

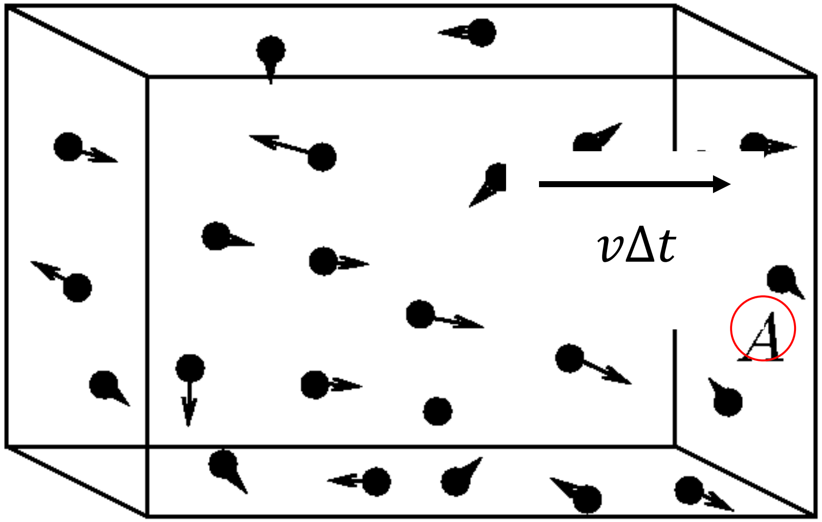
2.3.4. Kinetic Theory of Gases

- Molecular picture
  - Particle density: $N\,/\,V$
  - Only particles in defined sub-volume ($A \cdot v \cdot \Delta t$) have chance to hit wall within given time Δt
  - $1/3$ of velocity vectors statistically perpendicular to surface A
  - $1/2$ of them pointing towards wall
  - Number of collisions: $\frac{N}{V} \cdot \frac{1}{6} \cdot (\, A \times v \times \Delta t\,)$
  - Each particle transfers twice its momentum: $2 \cdot mv = F \cdot \Delta t$

$$\sum mv_i = \frac{N}{V} \cdot (A \cdot v \cdot \Delta t) \cdot \frac{1}{3} \cdot \frac{1}{2} \cdot (2mv)$$

$$= \frac{1}{3} \cdot \frac{N}{V} \cdot mv^2 \cdot A \cdot \Delta t$$

$$p = \frac{\bar{F}}{A} = \frac{1}{A} \cdot \frac{\overline{\sum mv}}{\Delta t} = \frac{N}{3V} \cdot m\overline{v^2}$$



2.3.4. Kinetic Theory of Gases

- Bernoulli equation

$$p = \frac{N}{3V} m\bar{v}^2$$

$$\overline{v_T^2} = \frac{3k_B T}{m}$$

  - By replacing v^2 with $\overline{v^2}$ (mean square velocity)
  - Substitute $\overline{v^2}$ by thermal velocity $\overline{v_T^2}$
- Equation of state for ideal gas
(applies to most gases under common conditions)

$$pV = Nk_B T$$ particles

$$pV = nR_g T$$ moles

  - # molecules N
  - # moles n
  - Gas constant $R_g = 8.31 \text{ J K}^{-1} \text{mol}^{-1}$

2.3.4. Kinetic Theory of Gases

- (Trivial) conclusions from equation of state
  - Law of Boyle-Mariotte

$$p \propto V^{-1} \text{ at } T = \text{const.}$$

  - Law of Gay-Lussac

$$p \propto T \text{ at } V = \text{const.}$$

  - Law of Charles

$$V \propto T \text{ at } p = \text{const.}$$

2.3.4. C_V and C_p for Gases

optional

- Heat capacity of gases
  - At constant volume
    - $C_V = \frac{1}{2} f N k_B$
  - At constant pressure
    - Volumetric expansion associated with mechanical work

$$E_N = \frac{f}{2} k_\mathrm{B} T$$

$$p\Delta V = pV\frac{\Delta T}{T} = Nk_\mathrm{B}T\frac{\Delta T}{T} = Nk_\mathrm{B}\Delta T$$

mech. work

heat

$$C_p = C_V + Nk_\mathrm{B} = \left(\frac{f}{2} + 1\right) Nk_\mathrm{B}$$

2.3.4. Adiabatic Change of Condition

- Adiabatic process
  - No exchange of thermal energy $Q = 0$
  - E.g., under thermal insulation → $\Delta U = -W$

$$\Delta U = Q - W$$

$$C \cdot \mathrm{d}T = -p\mathrm{d}V$$

  - Complete conversion (internal) heat ⇔ pneumatic work

- Insertion of equation of state and C_V

$$pV = Nk_\mathrm{B}T$$

$$\frac{f}{2}\frac{\mathrm{d}T}{T} = -\frac{\mathrm{d}V}{V}$$

$$C_V = ½ f N k_B$$

2.3.4. Adiabatic Change of Condition

optional

- Relationship for adiabatic process

$$V \propto T^{-f/2} \propto T^{1/(1-\gamma)}$$

  - Adiabatic coefficient

$$\gamma = \frac{C_p}{C_V} = \frac{f+2}{f} > 1$$

- Poisson equations

$$p \propto V^{-(f+2)/f} = V^{-\gamma}$$

$$p \propto T^{f/2+1} = T^{\gamma/(\gamma-1)}$$

  - Compare to „non-adiabatic“ gas laws

„non-adiabatic“ gas laws

$$V \propto T \text{ at } p = \text{const.}$$

$$p \propto V^{-1} \text{ at } T = \text{const.}$$

$$p \propto T \text{ at } V = \text{const.}$$

2.3.4. Mean Free Path

optional

- Collisional cross section for given gas

$$\sigma_{\text{coll}} \simeq \pi r_0^2$$

- Mean free path scales with
  - Inverse of particle density
  - Inverse of collisional cross-section of particles

$$l_{\text{mfp}} = \frac{1}{\sqrt{2}\varrho_N \sigma_{\text{coll}}}$$

thermal motion of targets

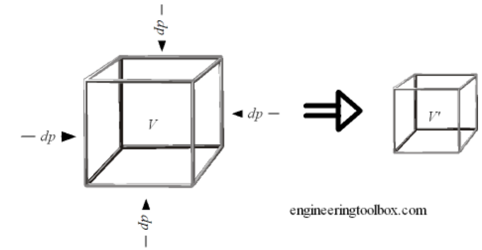
- Example: H_2 at $p = 1013\ \text{hPa}$
  - $l_{\text{mfp}} = 270\ \text{nm}$

2.3. Thermodynamics

2.3.5. Compressibility of Gases

- Compressibility of fluids

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p} = \frac{1}{\varrho_0}\frac{\partial \varrho}{\partial p}$$



  - Isothermal compressibility for ideal gas
  - Bulk modulus

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

$$pV = Nk_\mathrm{B}T$$

$$\hat{K} = \frac{1}{\kappa} = -V\frac{\partial p}{\partial V}$$

$$p\,V^\gamma = \text{const.}$$

- Differentiation of modified (adiabatic) law of Boyle-Mariotte

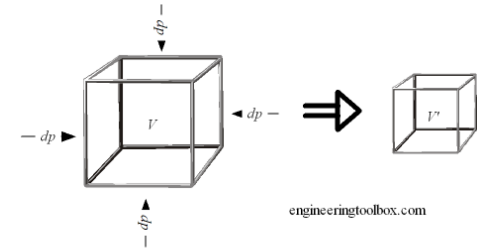
$$p\gamma V^{\gamma-1}\mathrm{d}V + V^\gamma \mathrm{d}p = 0$$

  - Adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_S = \frac{1}{\gamma p}$$

2.3.5. Compressibility of Liquids

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p} = \frac{1}{\varrho_0}\frac{\partial \varrho}{\partial p}$$



substance	κ in 10^{-11} Pa^{-1}
acetone	126
benzol	90
ethanol	110
glycerine	28
methanol	120
oil	47
mercury	4
water	46

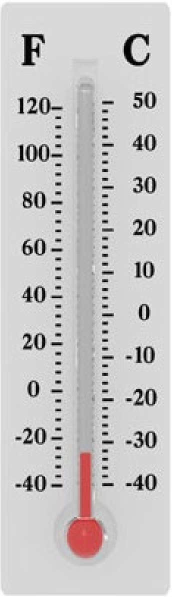
Table 2.1. Compressibility of liquids at $T = 20^\circ$C

2.3. Thermodynamics

2.3.6. Thermal Expansion

- Thermal expansion coefficient

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



- Gases: Derivation from equation of state for (ideal) gases

$$\alpha_V = \frac{1}{V}\frac{nR_g}{p}$$

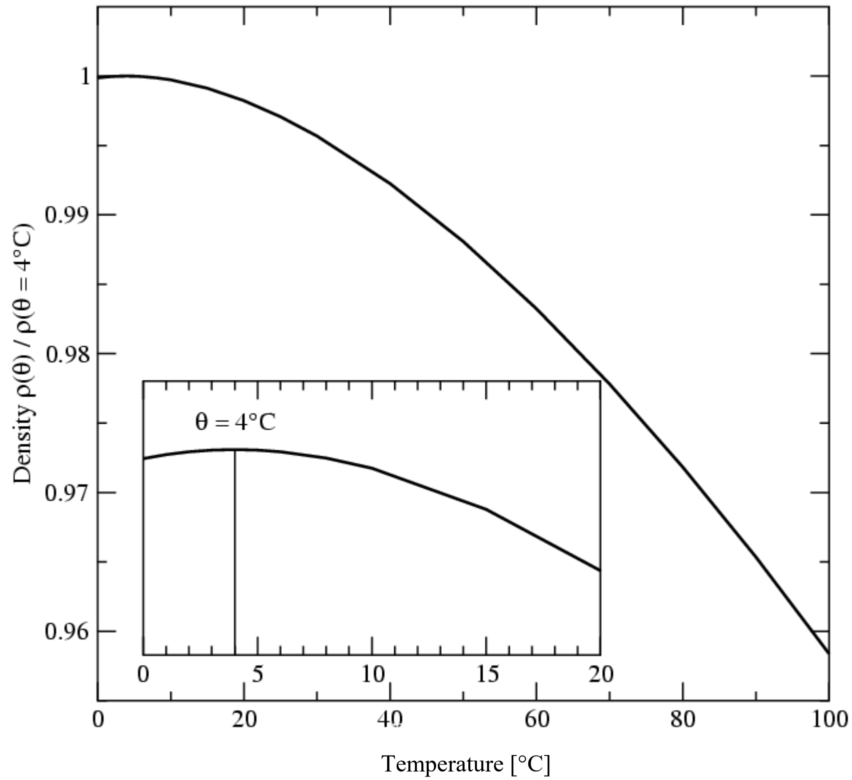
- Expansion of cube
  - Linear approximation

$$V(T) = V_0(1 + \alpha_V T)$$

liquid	$\alpha_V/10^{-5}\,\mathrm{K}^{-1}$
acetone	143
ethanol	143
benzol	106
mercury	18.1

Table 2.1. Thermal expansion coefficients of some liquids

2.3.6. Thermal Expansion – Anomaly of Water



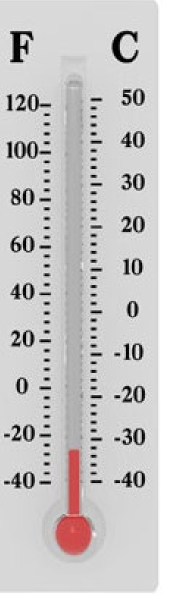


Fig. 2.4. Anomaly of water with the highest density reached at 4 K above its melting point

2.3. Thermodynamics

2.3.1. Heat and Temperature

2.3.2. Heat Capacity

2.3.3. Chemical Potentials

2.3.4. Kinetic Theory of Gases

2.3.5. Compressibility

2.3.6. Thermal Expansion

2.3.7. Real Gases

2.3.8. Vapor Pressure

2.3.7. Real Gases

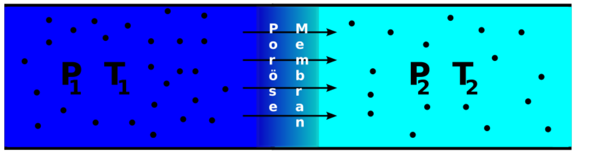
- Van-der-Waals equation

$$pV = nR_gT$$

$$\left(p + \frac{a}{V_n^2}\right)(V_n - b) = R_gT$$

- ➢ Volume per mole V_n
- ➢ „Internal pressure“ $a/V_n{}^2$
  - Attractive forces between molecules
- ➢ Parameter for strength of interaction a
- ➢ Covolume b
  - Spatial extension of molecules subtracted from overall volume
  - At low pressures negligible due to large volume per mole V_n

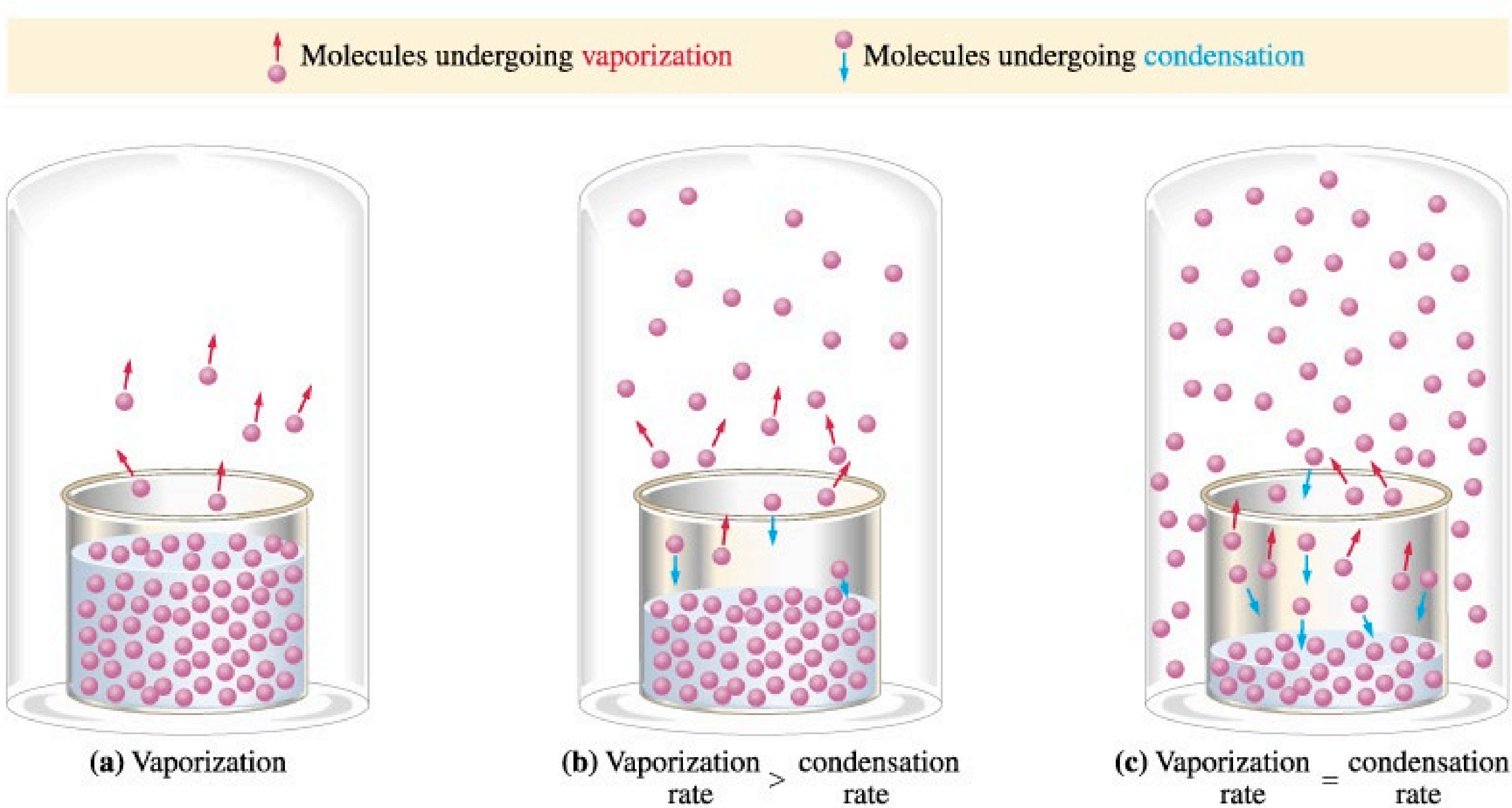
Joule-Thomson



- Joule-Thomson effect
  - ➢ Change in temperature (cooling) during rapid expansion
  - ➢ Work against intermolecular forces

2.3. Thermodynamics

2.3.8. Vapour Pressure



2.3.8. Vapor Pressure

- Coexistence of liquid and gaseous state
  - Closed vessel
  - Vapor forms above liquid
  - Saturated vapor pressure
  - Boiling

liquid	p_{vap} / hPa
water	23.3
ethanol	58.8
methanol	125
mercury	1.6×10^{-3}

Table 2.1. Saturated vapor pressure of some liquids at $\theta = 20°\mathrm{C}$

- Temperature dependence

$$p_{\mathrm{vap}} = \mathcal{B} e^{-\frac{\Delta E}{k_B T}}$$

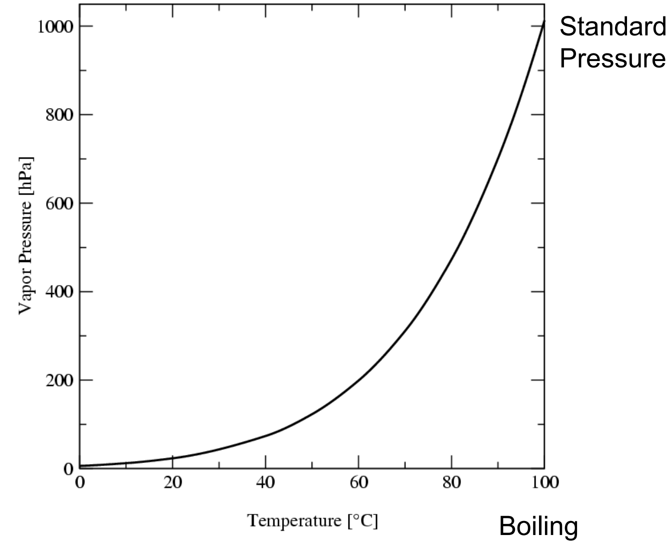


Fig. 2.5. Vapor pressure curve of water between $\theta = 0$ and $100°\mathrm{C}$

2.3.8. Vapor Pressure

optional

- Vapor pressure curve
  - ➢ Coexistence of liquid and vapor
  - ➢ Restricted to 1-dimensional curve
    - Above only vapor
    - Below only liquid
- Critical point
  - ➢ Phases „converge“

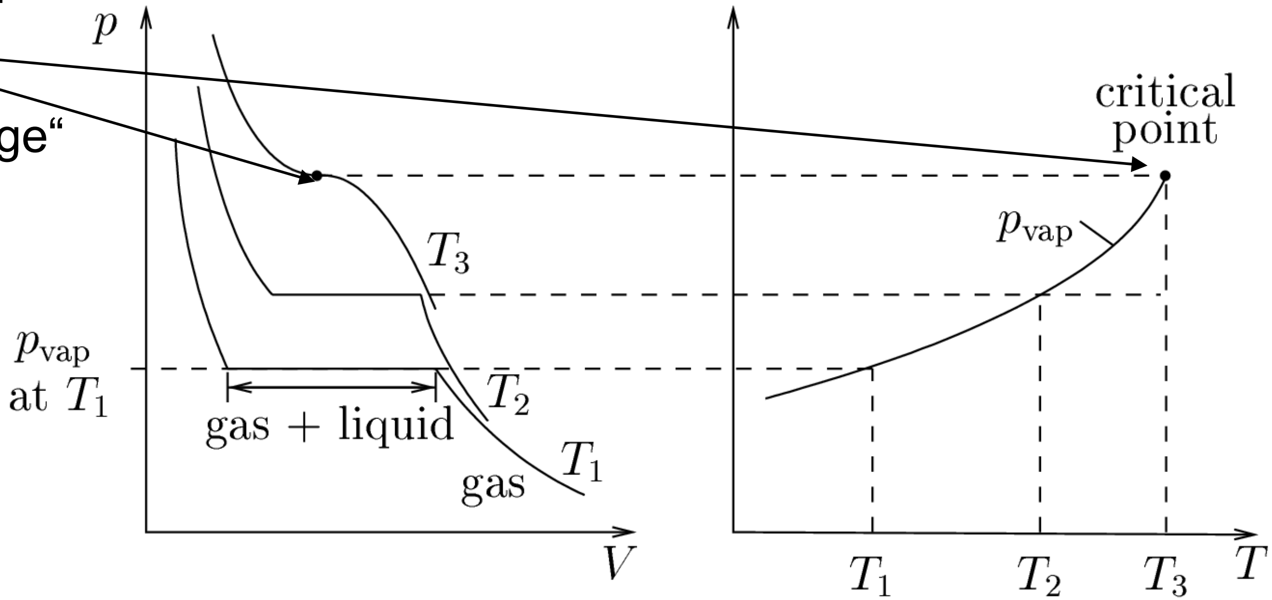


Fig. 2.6. Vapor pressure curves at three different temperatures T_i. The regions of constant slope in the (p, V)-diagram denote coexistence of the liquid and gaseous state, above the critical temperature T_3 the two phases can no longer be distinguished

2.3.8. Absolute Humidity

- Absolute humidity Φ_{abs}
  - Concentration of mass, measured in $\mathrm{g} / \mathrm{m}^3$
  - Relation to partial pressure of water p_{water}

$$p_{\mathrm{water}} = \varrho_{N,\mathrm{water}} k_{\mathrm{B}} T = \frac{\phi}{m_{\mathrm{water}}} k_{\mathrm{B}} T$$

  - Mass of water molecule m_{water}

- Relative humidity
  - Φ_{rel} referred to Φ_{abs} at saturation

Clouds in rain forest

Atacama desert

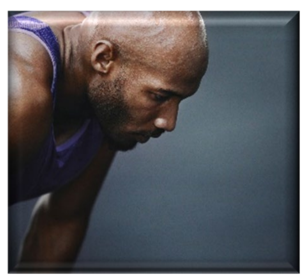
2.3.8. Heat of Vaporization

- Heat of vaporization Λ
- ΔE per mass to „escape“ liquid phase
  - Equation of **Clausius and Clapeyron**

$$\Lambda = T \frac{\mathrm{d}p}{\mathrm{d}T} \left[V_m(\text{vapor}) - V_m(\text{liquid}) \right]$$

  - Volume per mass V_m
  - Slope of vapor pressure curve dp/dT
  - Absolute temperature T

- Examples
  - Sweating
  - Refrigerator
  - Air-to-water heat pump



Summary: Important Formulas

- Thermal energy per molecule

$$\bar{E}_{\mathrm{kin}} = \frac{3}{2} k_{\mathrm{B}} T$$

- Specific heat capacity

$$C_m = \frac{C}{m} = \frac{\Delta E}{m \Delta T} = \frac{f}{2M} k_{\mathrm{B}}$$

- Gibbs free enthalpy

$$\Delta G = \Delta H - T \Delta S$$

- Pressure

$$p = \frac{F_{\perp}}{A}$$

- Equation of state for ideal gas

$$pV = n R_{\mathrm{g}} T$$

- Vapor pressure

$$p_{\mathrm{vap}} = \mathcal{B} \mathrm{e}^{-\frac{\Delta E}{k_{\mathrm{B}} T}}$$