

# Physical Chemistry lecture

2.1.1

## THERMODYNAMICS



### Part 2. Basic concepts

- 2.1.1. Thermodynamic system
- 2.1.2. Thermodynamic parameters and transformations
- 2.1.3. Zero principle of thermodynamics
- 2.1.4. Temperature - meaning and measurement

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## 2.1.2

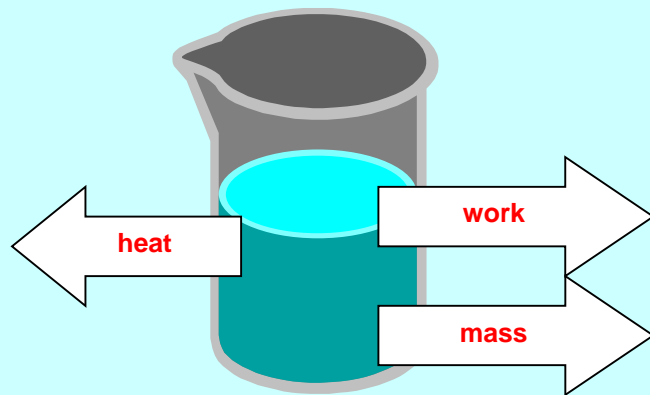
**Surroundings** - The surroundings are the part of space that does not belong to the system. Surroundings may include heat sources and containers of substances.

**Balance shield** - Provides a boundary between the system and the surroundings. Allows control of the amount of energy and substances flowing between the system and the surroundings.

types of balance shields:

diathermic shield - allows the flow of heat

adiabatic shield - prevents the flow of energy in the form of heat



open - exchange of mass and Energy

closed - no mass exchange, energy exchange possible

adiabatic - no heat exchange, mass exchange possible

insulated - no mass or energy exchange

**Thermodynamic system**

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graph TD; A[Thermodynamic system] --> B[single-component]; A --> C[multicomponent]; B --> D[single-phase]; B --> E[multi-phase]; C --> D; C --> E;
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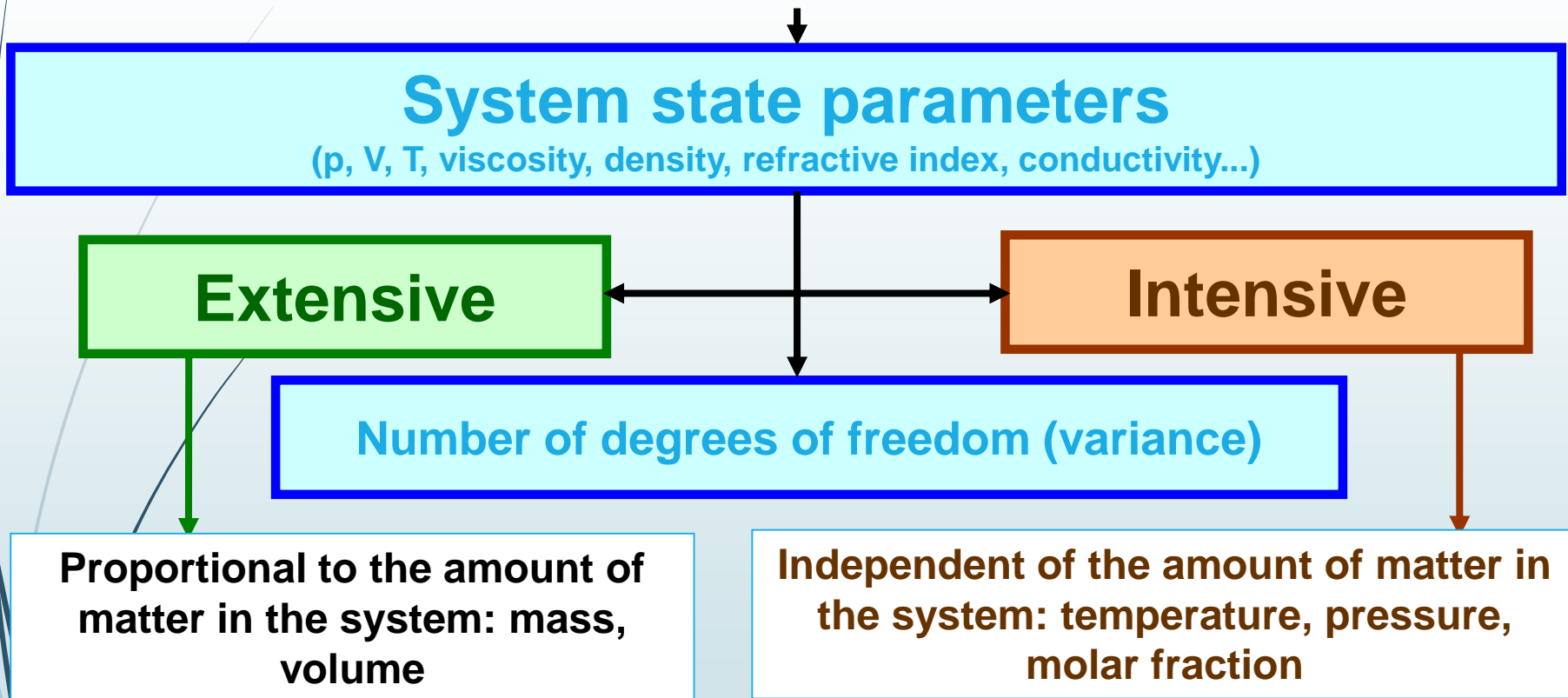
**single-component**

**multicomponent**

**single-phase**

**multi-phase**

# State of the thermodynamic system



Thermodynamic processes (thermodynamic transformation) - a phenomenon during which the value of at least one state parameter changes.

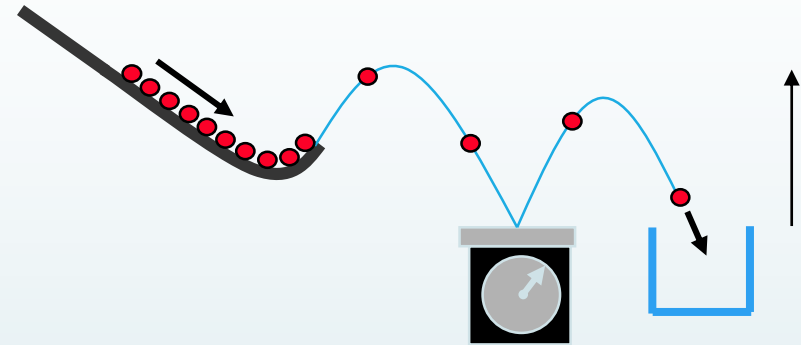
This is called a thermodynamic system transformation or briefly thermodynamic process.

## 2.1.5

## Thermodynamic state parameters

$$P = \frac{F}{A}$$

$$[Pa] = \left[ \frac{N}{m^2} \right]$$



**1 atm = 101.325 kPa = 1013.25 hPa = 1.01325 bar**

**1 atm = 760 mmHg  $\approx$  10 mH<sub>2</sub>O**

**1 bar = 1000hPa**

## 2.1.6

## Parametry termodynamiczne

Examples of temperature scales:

Thermodynamic temperature scale according to Kelvin's concept.

A theoretical scale based on the efficiency of the Carnot cycle. The unit of this scale is the Kelvin (K), the basic unit of the International System of Units SI.

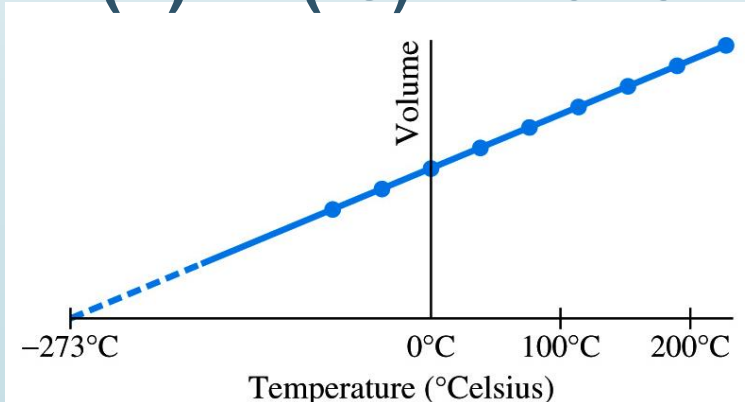
Celsius temperature scale.

An empirical scale first defined in 1743, based on two fixed points:  $t_1=0^\circ\text{C}$  (melting point of ice),  $t_2=100^\circ\text{C}$  (boiling point of water). Both of these points are defined at a pressure of  $101325\text{ N/m}^2$  [Pa] = 1 atmosphere. The unit is degrees Celsius ( $^\circ\text{C}$ ).

Fahrenheit temperature scale.

G. D. Fahrenheit (1714) perfected the mercury thermometer, built about 50 years earlier, and created the first temperature scale - an empirical temperature scale based on two fixed points:  $t_1=0^\circ\text{F}$  (snow-salmon mixing temperature) and  $t_2=100^\circ\text{F}$  (normal human body temperature). This scale is mainly used in countries using the English and American systems of measurement.

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$



Does T units matter?

$$\theta/^{\circ}\text{C} = T/\text{K} - 273.15$$

Definition of  
Celsius scale

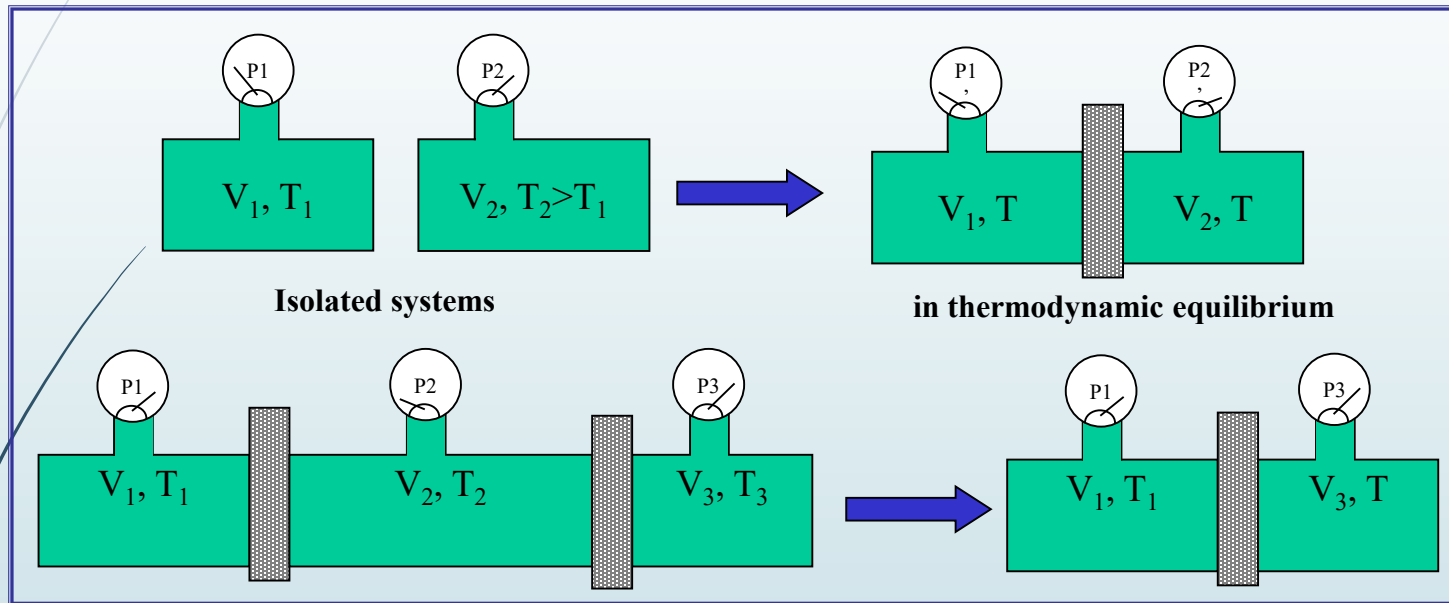
(F.2)

# Zero principle of thermodynamics

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If each of two systems is in thermal equilibrium with some third system, then these two systems are also in thermal equilibrium.

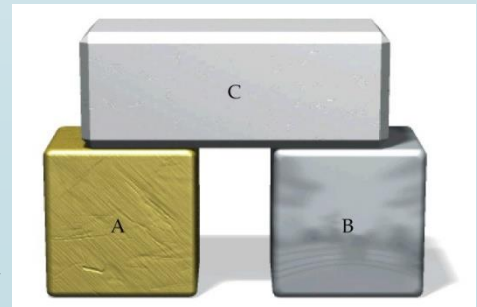
The zeroth principle of thermodynamics makes it possible to formulate a macroscopic definition of temperature. It can be said that temperature is a state parameter that has the same value for all bodies in thermal equilibrium. There can be an infinite number of thermal equilibrium states, with a different temperature corresponding to each of them.



If systems A and B are in thermal equilibrium with system C, they are also in thermal equilibrium with respect to each other.

E.A. Guggenheim, R. Fowler (1939)

law of transitory



# Microscopic interpretation of temperature

## 2.1.8

In the kinetic interpretation of gas theory, temperature is a measure of the average kinetic energy of the motion of the centres of mass of the particles.

$$E = \frac{f}{2} kT$$

f – number of internal degrees of freedom

### Energy resource levels at different degrees of freedom:

Distance between **electron** levels from 200 to 8000 kJ/mol

Distance between **oscillatory** levels 6 to 40 kJ/mol

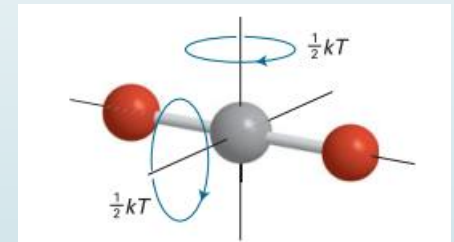
Distance between **rotational** levels 10-2 kJ/mol

Distance between **translational** levels 10-14 kJ/mol

Translational levels make continuous i.e. energy absorption/emission is continuous even small portions of energy can be converted into translational energy.

In a sample at a temperature  $T$ , all quadratic contributions to the total energy have the same mean value, namely  $\frac{1}{2}kT$ .

Equipartition theorem



Example: consequences for a perfect gas

$$C_V = \frac{3}{2} R$$

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

		$C_p$ (J/mol K)	$C_V$ (J/mol K)	$C_p - C_V$ (J/mol K)
Monatomic	Ideal	$\frac{5}{2}R = 20.79$	$\frac{3}{2}R = 12.47$	$R = 8.31$
Diatomic	Ideal	$\frac{7}{2}R = 29.10$	$\frac{5}{2}R = 20.79$	$R = 8.31$
Polyatomic	Ideal	$4R = 33.26$	$3R = 24.94$	$R = 8.31$



## 2.1.9

# Thermometers

Any physical property that changes monotonically and continuously (preferably linearly) with temperature can be used to measure temperature. Such a device is called a thermometer.

### Example: linear expansion



$$\Delta L/L = \alpha \Delta T$$

$$\frac{dL}{dT} = \alpha L$$

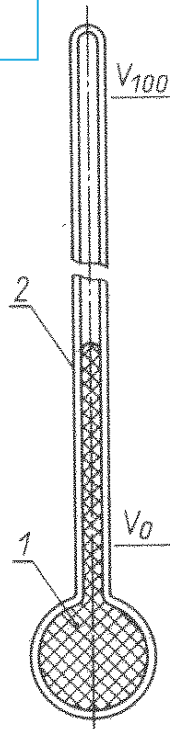
Expansion coefficients:

Aluminum :  $\alpha = 2.4 \times 10^{-5} \text{K}^{-1}$

Steel :  $\alpha = 1.2 \times 10^{-5} \text{K}^{-1}$

Glass :  $\alpha = 5 \times 10^{-6} \text{K}^{-1}$

Quartz :  $\alpha = 4 \times 10^{-7} \text{K}^{-1}$



### 1. Mercury,

Alcoholic measurement of changes in fluid volume for gas under constant pressure

$$T(V) = 273,15 \text{ K} \frac{V}{V_{tr}}$$

### 2. Bolometers

measurement of changes in the pressure of a gas confined in a constant volume

$$T(p) = 273,15 \text{ K} \frac{p}{p_{tr}}$$

### 3. Reed switch thermometers

measurement of changes in rod length

$$T(L) = 273,15 \text{ K} \frac{L}{L_{tr}}$$

# Termometry

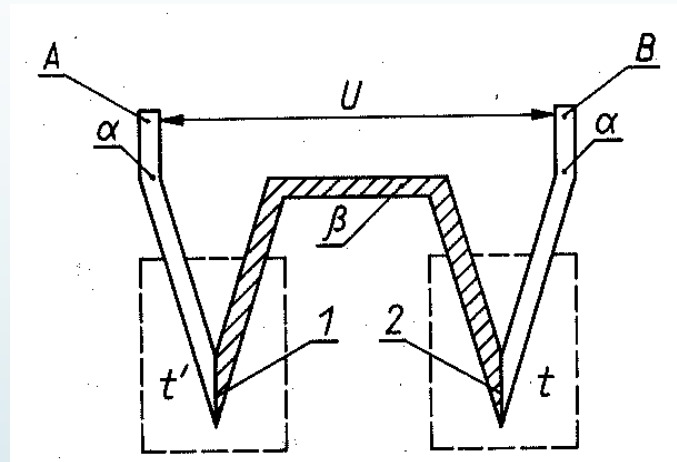
## 2.1. 10

### 4. Thermocouple - measurement of voltage changes

A thermocouple is a junction of two different metals, which produces a low voltage - most often in the millivolt range - and a temperature coefficient of  $50 \mu\text{V}/^\circ\text{C}$ . Using thermocouples, you can measure temperatures from  $-270^\circ\text{C}$  to  $+2700^\circ\text{C}$  with an error in the range of  $0.5\text{-}2^\circ\text{C}$ .

Principle of thermocouple construction

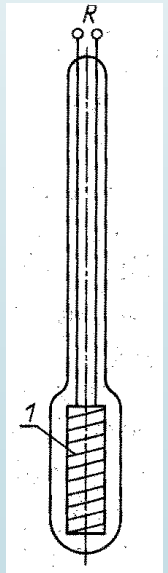
- 1 - reference weld
- 2 - measurement weld
- $\alpha, \beta$  - metals



### 5. Thermistors - electrical resistance of the wire

semiconductor resistive elements with a negative temperature coefficient of resistance, the value of which is approximately  $-4\%/^\circ\text{C}$ . Generally, thermistors with a resistance at room temperature of several  $\text{k}\Omega$  are used. Thermistors are very suitable for measuring temperature and controlling its changes in the range from  $-50^\circ\text{C}$  to  $+300^\circ\text{C}$  with an error not exceeding  $0.1$  to  $0.2^\circ\text{C}$ .

$$T(R) = 273,15\text{K} \frac{R}{R_0}$$



# Termometry

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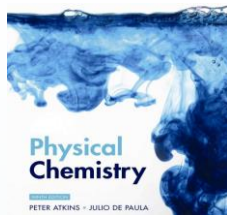
## 6. Pyrometers – emission spectrum

measurement of changes in electromagnetic radiation emissions is achieved by observing a glowing object through a telescope and comparing its color with the color of the glow wire placed inside the pyrometer. Optical pyrometers measure temperatures ranging from  $750^{\circ}\text{C}$  to  $+3000^{\circ}\text{C}$ . The error is estimated at about  $4^{\circ}\text{C}$  near the lower limit of the measurement range and about  $20^{\circ}\text{C}$  near the upper limit. Infrared pyrometers are more accurate.



Thermal imaging camera,  
infrared pyrometer





## F.4 Energy

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**Key points** (a) Energy is the capacity to do work. (b) The total energy of a particle is the sum of its kinetic and potential energies. The kinetic energy of a particle is the energy it possesses as a result of its motion. The potential energy of a particle is the energy it possesses as a result of its position. (c) The Coulomb potential energy between two charges separated by a distance  $r$  varies as  $1/r$ .

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## F.5 The relation between molecular and bulk properties

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**Key points** (a) The energy levels of confined particles are quantized. (b) The Boltzmann distribution is a formula for calculating the relative populations of states of various energies. (c) The equipartition theorem provides a way to calculate the energy of some systems.

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## F.7 Units

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**Key points** (a) The measurement of a physical property is expressed as the product of a numerical value and a unit. (b) In the International System of units (SI), the units are formed from seven base units, and all other physical quantities may be expressed as combinations of these physical quantities and reported in terms of derived units.

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# Lets play a bit ....

## Exercises

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**Table F.2** A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	$1 \text{ kg m s}^{-2}$	newton, N
Pressure	$1 \text{ kg m}^{-1} \text{ s}^{-2}$ $1 \text{ N m}^{-2}$	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{ s}^{-2}$ $1 \text{ N m}$ $1 \text{ Pa m}^3$	joule, J
Power	$1 \text{ kg m}^2 \text{ s}^{-3}$ $1 \text{ J s}^{-1}$	watt, W

\* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

**Table F.3** Common SI prefixes

Prefix	y	z	a	f	p	n	$\mu$	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	$10^{-24}$	$10^{-21}$	$10^{-18}$	$10^{-15}$	$10^{-12}$	$10^{-9}$	$10^{-6}$	$10^{-3}$	$10^{-2}$	$10^{-1}$
Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	$10^2$	$10^3$	$10^6$	$10^9$	$10^{12}$	$10^{15}$	$10^{18}$	$10^{21}$	$10^{24}$

**Table F.4** Some common units

Physical quantity	Name of unit	Symbol for unit	Value*
Time	minute	min	60 s
	hour	h	3600 s
	day	d	86 400 s
	year	a	31 556 952 s
Length	ångström	Å	$10^{-10} \text{ m}$
Volume	litre	L, l	$1 \text{ dm}^3$
Mass	tonne	t	$10^3 \text{ kg}$
Pressure	bar	bar	$10^5 \text{ Pa}$
	atmosphere	atm	101.325 kPa
Energy	electronvolt	eV	$1.602 176 53 \times 10^{-19} \text{ J}$
			96.485 31 kJ mol <sup>-1</sup>

\* All values in the final column are exact, except for the definition of 1 eV, which depends on the measured value of  $e$ , and the year, which is not a constant and depends on a variety of astronomical assumptions.

## F.3 Bulk matter

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**F3.1(a)** Compare and contrast the properties of the solid, liquid, and gas states of matter.

**F3.1(b)** Compare and contrast the properties of the condensed and gaseous states of matter.

**F3.2(a)** Classify the following properties as extensive or intensive: (a) mass, (b) mass density, (c) temperature, (d) number density.

**F3.2(b)** Classify the following properties as extensive or intensive: (a) pressure, (b) specific heat capacity, (c) weight, (d) molality.

**F3.1(b)** Condensed forms of matter (liquids and solids) have relatively high densities because of the close proximity of constituent elemental atoms or constituent molecules; compressibility is low and attractive forces are strong between neighbours. Perfect gases have low densities and they are highly compressible; intermolecular forces of attraction are negligibly small.

**F3.2(b)**

- (a) Pressure is an intensive property.
- (b) Specific heat capacity is an intensive property.
- (c) Weight is an extensive property.
- (d) Molality is an intensive property.

**F3.3(a)** Calculate (a) the amount of  $\text{C}_2\text{H}_5\text{OH}$  (in moles) and (b) the number of molecules present in 25.0 g of ethanol.

**F3.3(b)** Calculate (a) the amount of  $\text{C}_6\text{H}_{12}\text{O}_6$  (in moles) and (b) the number of molecules present in 5.0 g of glucose.

$$\text{F3.3(b)} \quad (\text{a}) \quad n = \frac{m}{M} = 5.0 \text{ g} \left( \frac{1 \text{ mol}}{180.16 \text{ g}} \right) = \boxed{0.028 \text{ mol}} \quad [\text{F.1}]$$

$$(\text{b}) \quad N = nN_A = 0.028 \text{ mol} \left( \frac{6.0221 \times 10^{23} \text{ molecules}}{\text{mol}} \right) = \boxed{1.7 \times 10^{22} \text{ molecules}}$$

**F3.4(a)** Express a pressure of 1.45 atm in (a) pascal, (b) bar.

**F3.4(b)** Express a pressure of 222 atm in (a) pascal, (b) bar.

**F3.5(a)** Convert blood temperature, 37.0°C, to the Kelvin scale.

**F3.5(b)** Convert the boiling point of oxygen, 90.18 K, to the Celsius scale.

$$\text{F3.4(b)} \quad \text{(a)} \quad (222 \text{ atm}) \times \left( \frac{101325 \text{ Pa}}{1 \text{ atm}} \right) = 2.25 \times 10^7 \text{ Pa}$$

(b) Since 1 bar =  $10^5$  Pa, the above pressure is 225 bar.

$$\text{F3.5(b)} \quad \theta/^{\circ}\text{C} = T/\text{K} - 273.15 = 90.18 - 273.15 = -182.97 \text{ [F.2]}$$

$$\theta = -182.97 \text{ }^{\circ}\text{C}$$

## F.4 Energy

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**F4.1(a)** Define energy and work.

**F4.1(b)** Distinguish between kinetic and potential energy.

**F4.2(a)** Consider a region of the atmosphere of volume  $25 \text{ dm}^3$  that at  $20^\circ\text{C}$  contains about  $1.0 \text{ mol}$  of molecules. Take the average molar mass of the molecules as  $29 \text{ g mol}^{-1}$  and their average speed as about  $400 \text{ m s}^{-1}$ . Estimate the energy stored as molecular kinetic energy in this volume of air.

**F4.2(b)** Calculate the minimum energy that a bird of mass  $25 \text{ g}$  must expend in order to reach a height of  $50 \text{ m}$ .

**F4.2(b)** The law of conservation of energy requires that the minimum kinetic energy [F.4] required to reach height  $h$  equals the increase in gravitational potential energy [F.5]:

$$E_k = mgh$$

$$= (0.025 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (50 \text{ m}) = 12 \text{ kg m}^2 \text{ s}^{-2} = \boxed{12 \text{ J}}$$

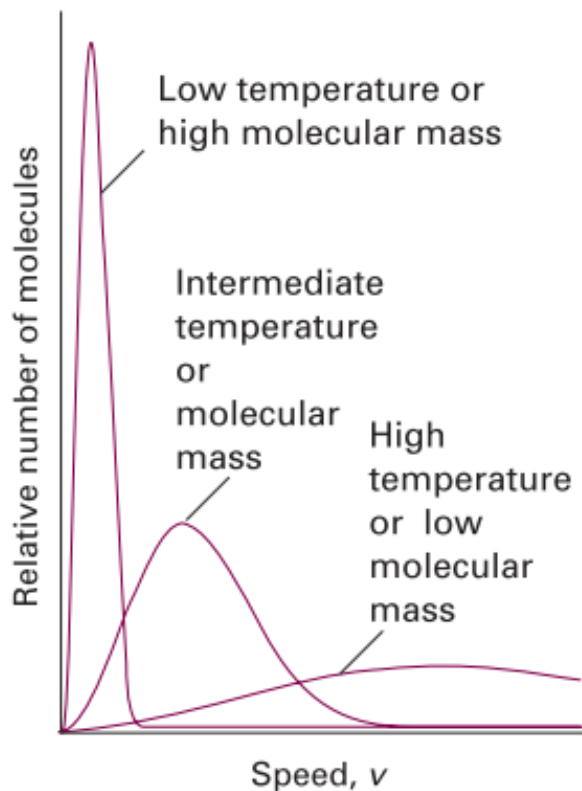


**F5.5(a)** Calculate the relative mean speeds of  $N_2$  molecules in air at  $0^\circ\text{C}$  and  $40^\circ\text{C}$ .

**F5.5(b)** Calculate the relative mean speeds of  $\text{CO}_2$  molecules in air at  $20^\circ\text{C}$  and  $30^\circ\text{C}$ .

## Maxwell distribution,

$$v_{\text{mean}} \propto \left(\frac{T}{M}\right)^{1/2} \quad (\text{F.11})$$



$$\text{F5.5(b)} \quad v_{\text{mean}} \propto (T/M)^{1/2} \quad [\text{F.11}]$$

$$\frac{v_{\text{mean}}(T_2)}{v_{\text{mean}}(T_1)} = \frac{(T_2/M)^{1/2}}{(T_1/M)^{1/2}} = \left(\frac{T_2}{T_1}\right)^{1/2}$$

$$\frac{v_{\text{mean}}(303 \text{ K})}{v_{\text{mean}}(293 \text{ K})} = \left(\frac{303 \text{ K}}{293 \text{ K}}\right)^{1/2} = \boxed{1.02}$$

Fig. F.7 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

Do not ommit ....

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*MATHEMATICAL BACKGROUND 1*

**Differentiation and integration**

*MATHEMATICAL BACKGROUND 2*

**Multivariate calculus**