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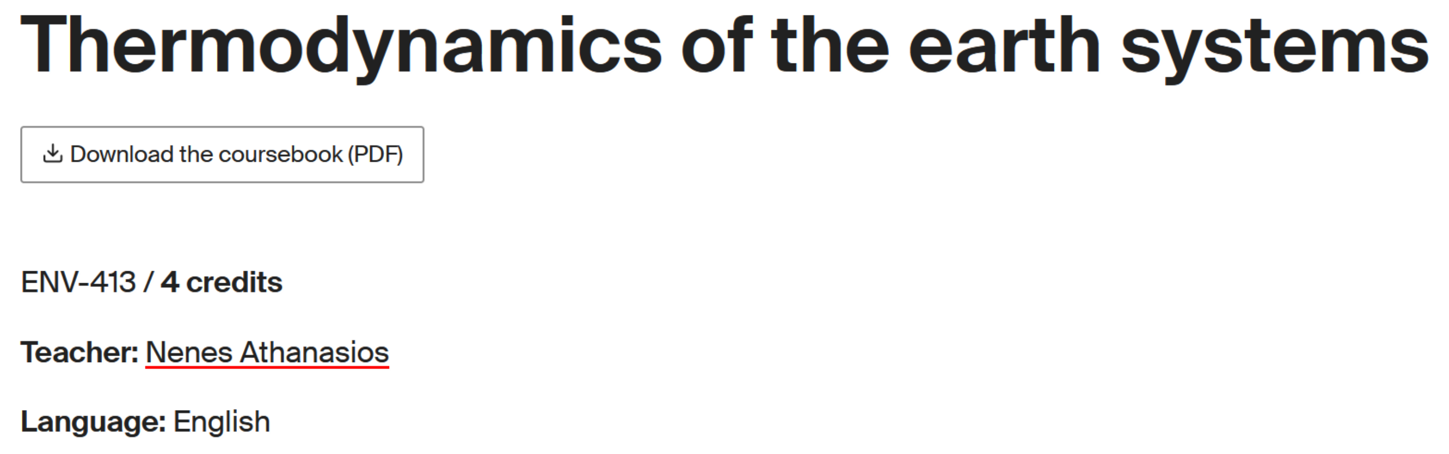


Thermodynamics of the earth systems

ENV-413 / **4 credits**

Teacher: Nenes Athanasios

Language: English

Athanasios Nenes

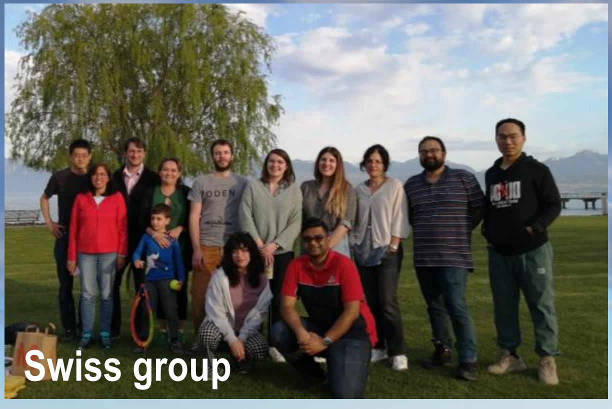
Teaching Assistant
Romanos Foskinis

EPFL

FORTH C-STACC Center for the Study of Air Quality & Climate Change

LAPI – Athanasios (Thanos) Nenes

Laboratory of atmospheric processes and their impacts


Swiss group


Greek group

http://lapi.epfl.ch

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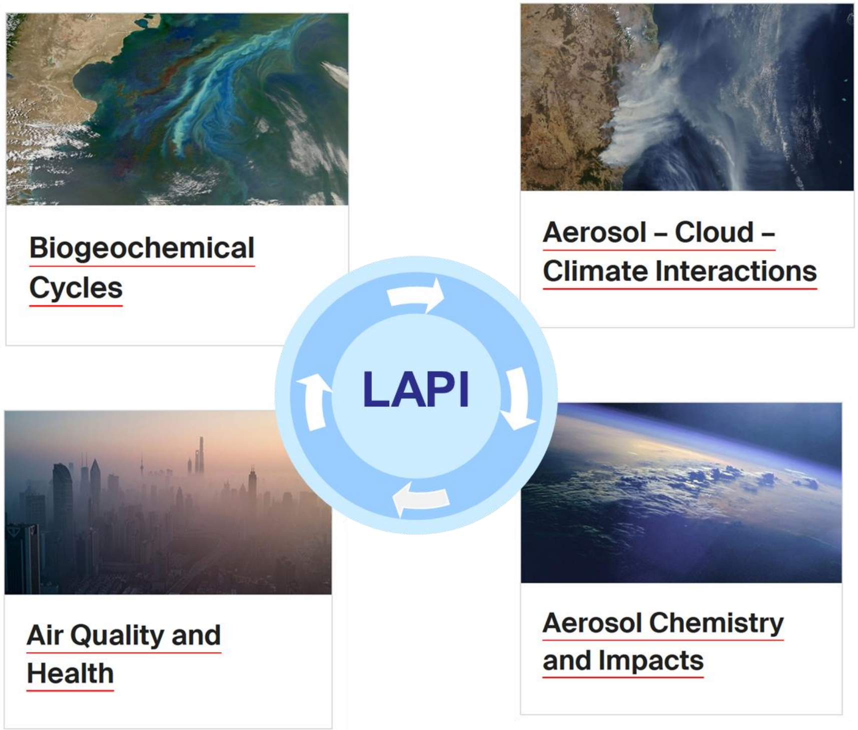

iMIRACLI

CleanCloud

FORCeS

ReCLEAN

GREEN FJORD

LIPIC Air

erc European Research Council Established by the European Commission

EASVOLEE

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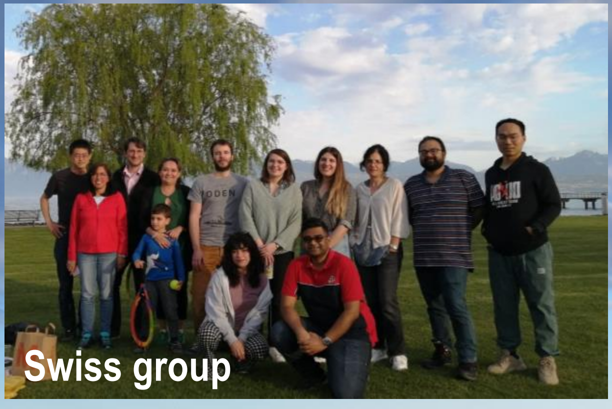
Laboratory of atmospheric processes and their impacts



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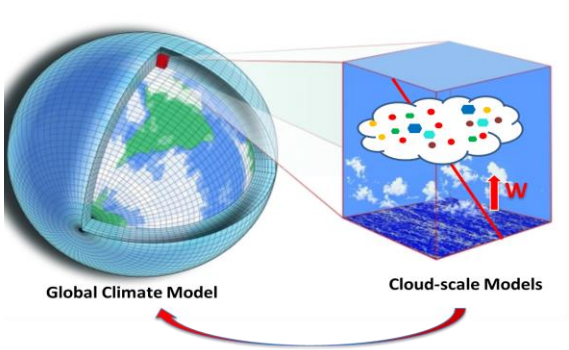
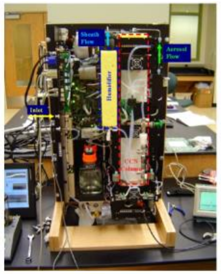
Field and Laboratory Observations

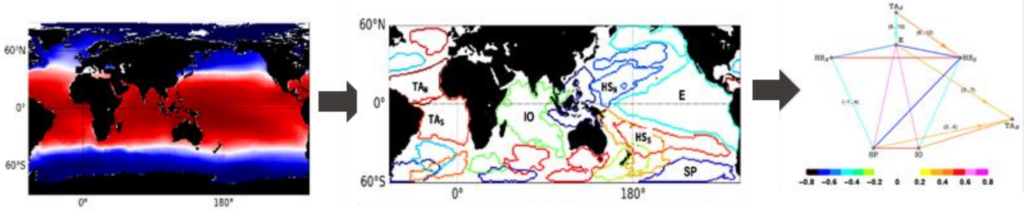
Modeling



Instrumentation



Cloud Condensation Nuclei Counter, US Patent 7,656,510



Data science

Class Objectives & Philosophy

Potential Grading Scheme:

Project: 25%; Final exam: 75%

Course Objectives, Teaching Philosophy:

- Apply thermodynamic principles to understand the role of water in the Earth System.
- Broad conceptual framework for understanding the thermodynamics of oceans and atmospheres, so material can be integrated into other study disciplines.
- Students are expected to read the assigned material before class.
- Class time will be used for lecturing, with the purpose of emphasizing points of the material, or, going through other aspects not directly covered by the textbook.
- “Collaborative learning" approach will often be used, students working in teams use class time for worksheets that include quizzes, problem-solving and discussions. Students are expected to work in teams on the worksheets (both in class and homework).

Material covered in Lecture 1

Part 1: Introduction

Introduction

- Thermodynamic systems: composition and state; system vs the environment; open or closed or isolated; boundaries of a system and the environment,
- Thermodynamic state and properties of a system: state variables (intensive and extensive). thermodynamic properties

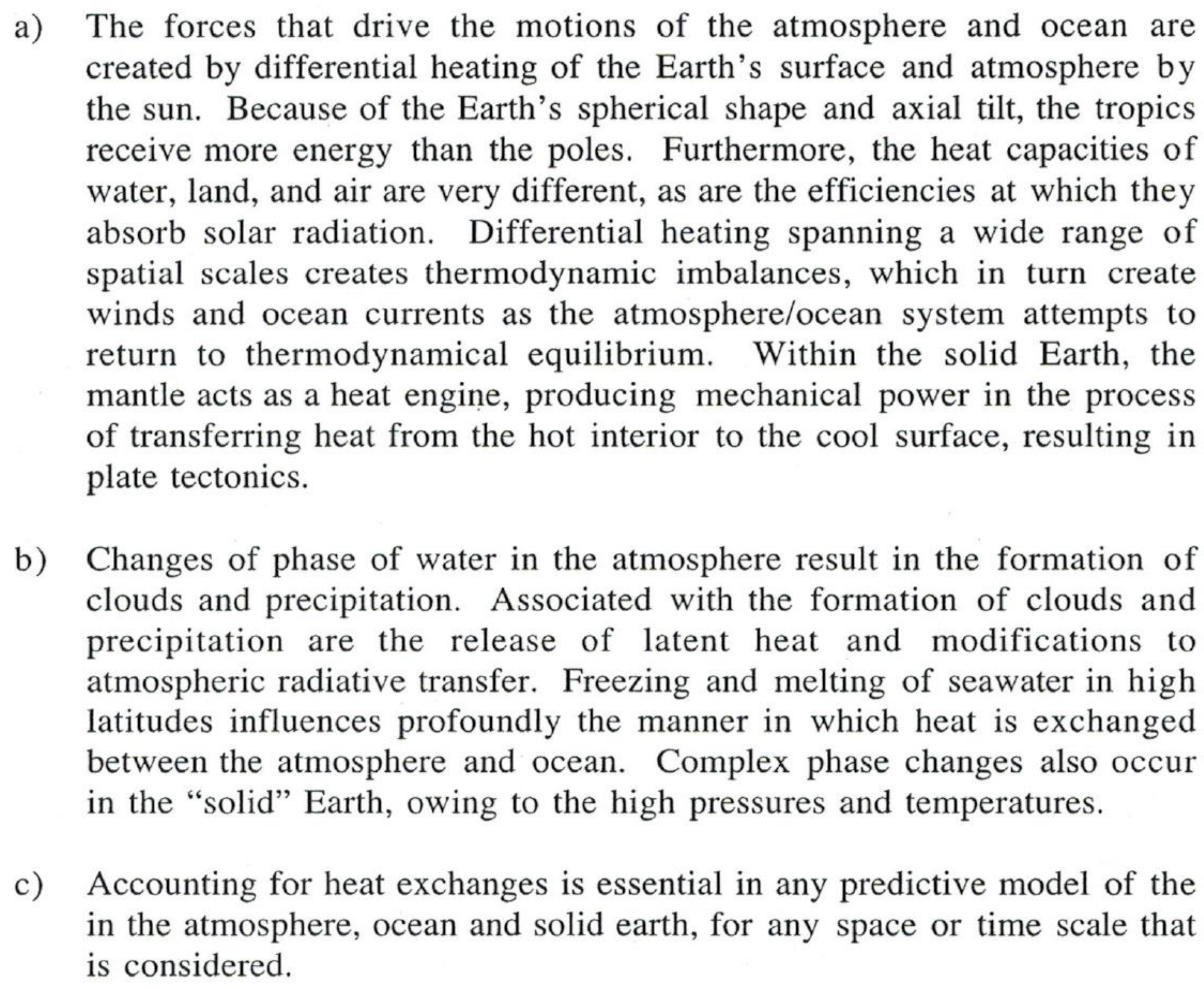
Composition, structure of components of the earth system

- Composition: atmosphere, ocean, solid earth
- Pressure, Density, Temperature; variations in the atmosphere, ocean, solid earth;
- Hydrostatic equation: application to ocean and hypothetical constant density atmosphere; solid earth

Equation of state

- Ideal gas law
- Kinetic-molecular model of the ideal gas
- Equation of state for air: Dalton's law of partial pressures; virtual temperature
- Hypsometric equation (atmosphere)
- Equation of state for real gases, liquids, and solids
- Equation of state for seawater

Why do we need Thermo?

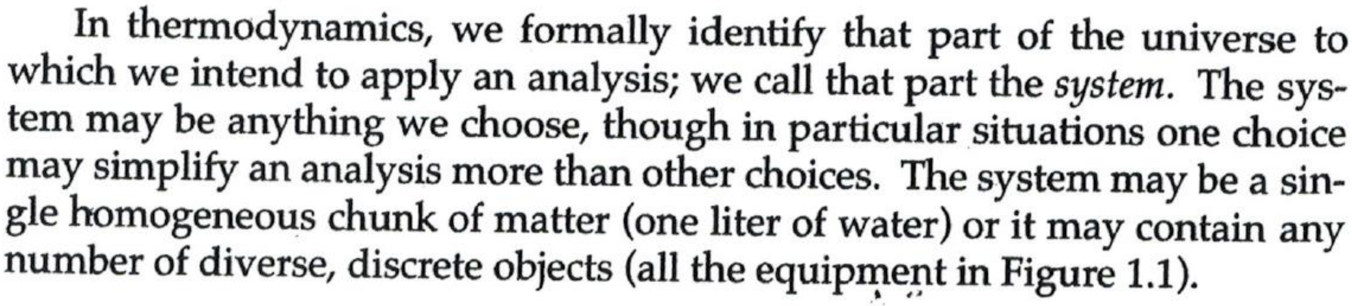


a) The forces that drive the motions of the atmosphere and ocean are created by differential heating of the Earth's surface and atmosphere by the sun. Because of the Earth's spherical shape and axial tilt, the tropics receive more energy than the poles. Furthermore, the heat capacities of water, land, and air are very different, as are the efficiencies at which they absorb solar radiation. Differential heating spanning a wide range of spatial scales creates thermodynamic imbalances, which in turn create winds and ocean currents as the atmosphere/ocean system attempts to return to thermodynamical equilibrium. Within the solid Earth, the mantle acts as a heat engine, producing mechanical power in the process of transferring heat from the hot interior to the cool surface, resulting in plate tectonics.

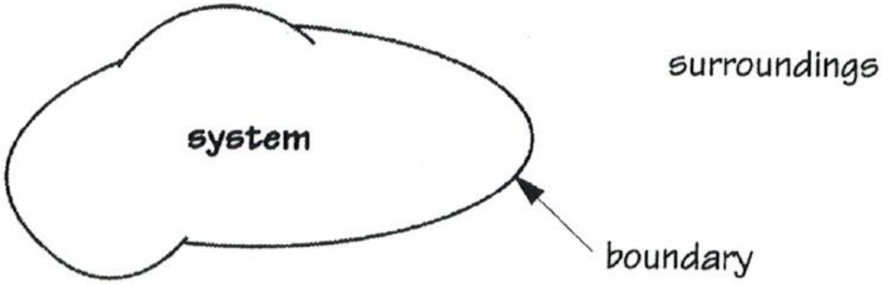
b) Changes of phase of water in the atmosphere result in the formation of clouds and precipitation. Associated with the formation of clouds and precipitation are the release of latent heat and modifications to atmospheric radiative transfer. Freezing and melting of seawater in high latitudes influences profoundly the manner in which heat is exchanged between the atmosphere and ocean. Complex phase changes also occur in the "solid" Earth, owing to the high pressures and temperatures.

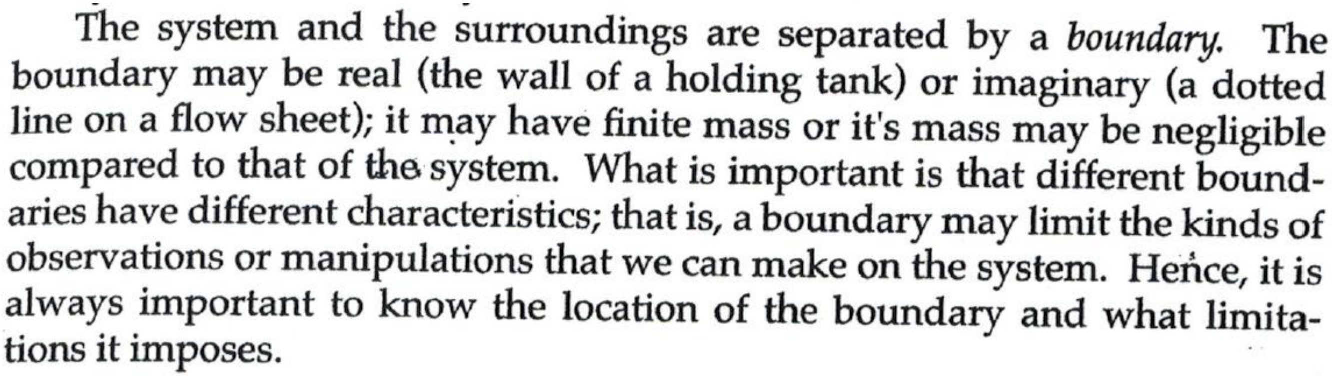
c) Accounting for heat exchanges is essential in any predictive model of the in the atmosphere, ocean and solid earth, for any space or time scale that is considered.

Basic concepts: System



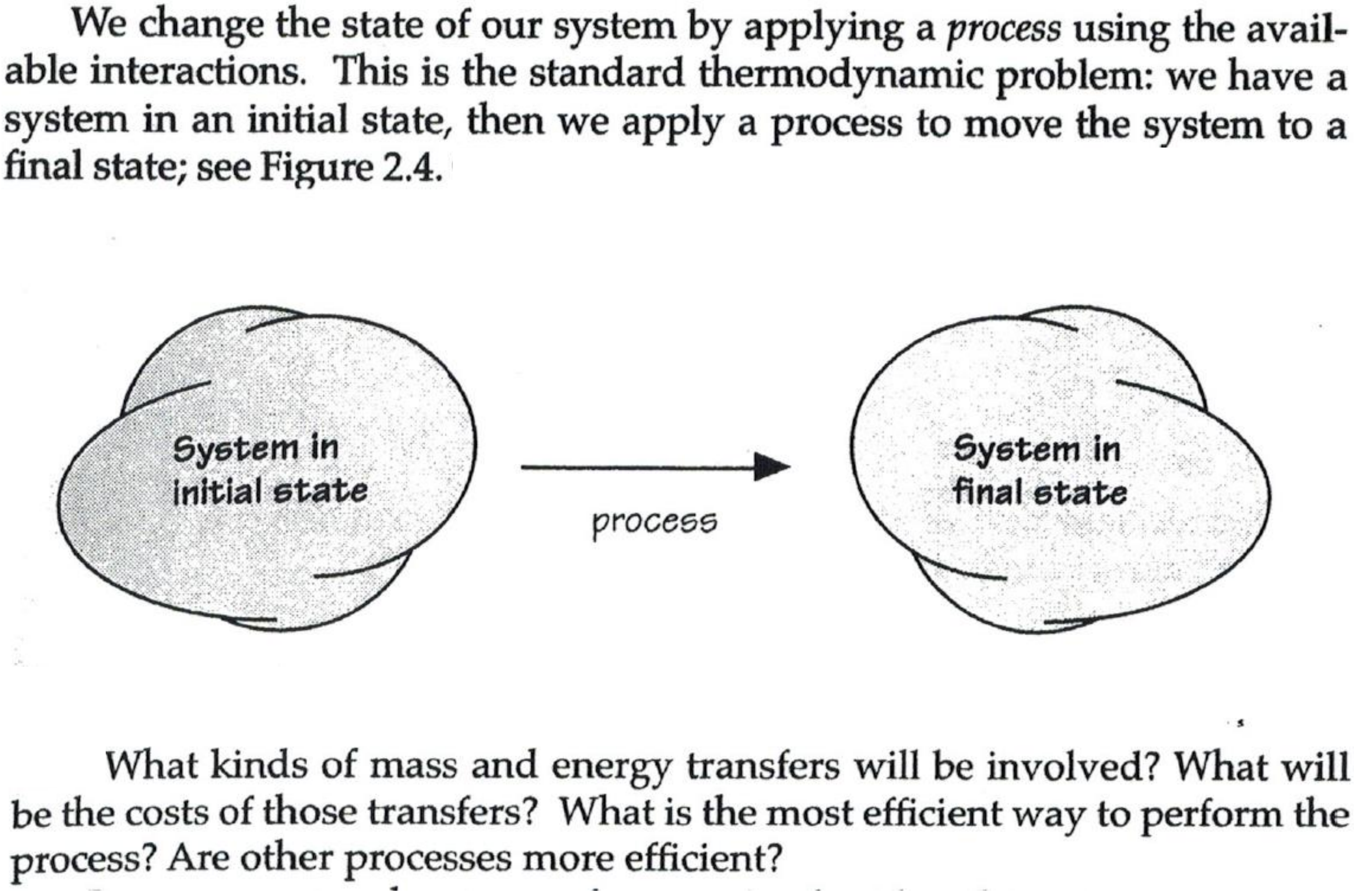
In thermodynamics, we formally identify that part of the universe to which we intend to apply an analysis; we call that part the *system*. The system may be anything we choose, though in particular situations one choice may simplify an analysis more than other choices. The system may be a single homogeneous chunk of matter (one liter of water) or it may contain any number of diverse, discrete objects (all the equipment in Figure 1.1).





The system and the surroundings are separated by a *boundary*. The boundary may be real (the wall of a holding tank) or imaginary (a dotted line on a flow sheet); it may have finite mass or it's mass may be negligible compared to that of the system. What is important is that different boundaries have different characteristics; that is, a boundary may limit the kinds of observations or manipulations that we can make on the system. Hence, it is always important to know the location of the boundary and what limitations it imposes.

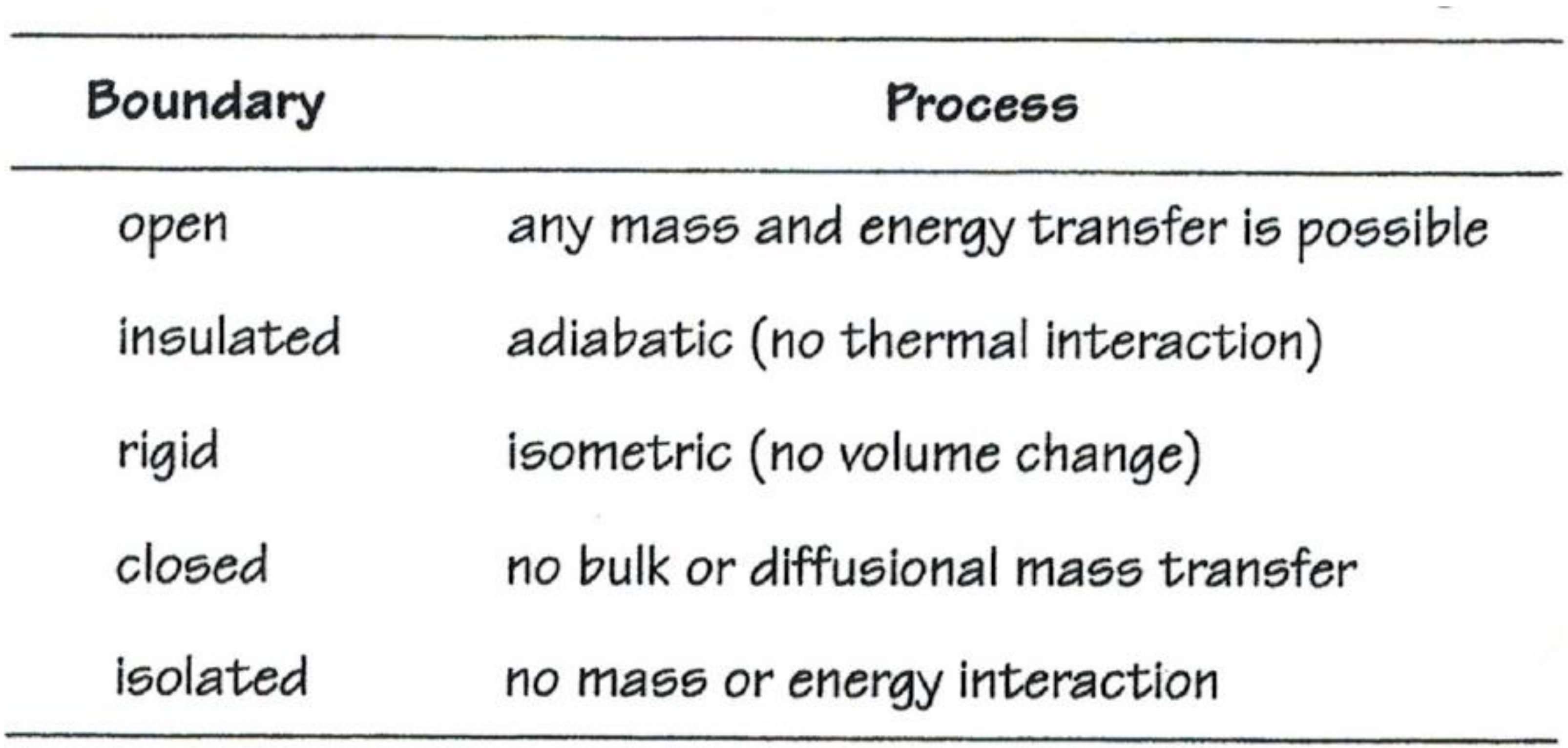
Basic concepts: processes



We change the state of our system by applying a *process* using the available interactions. This is the standard thermodynamic problem: we have a system in an initial state, then we apply a process to move the system to a final state; see Figure 2.4.

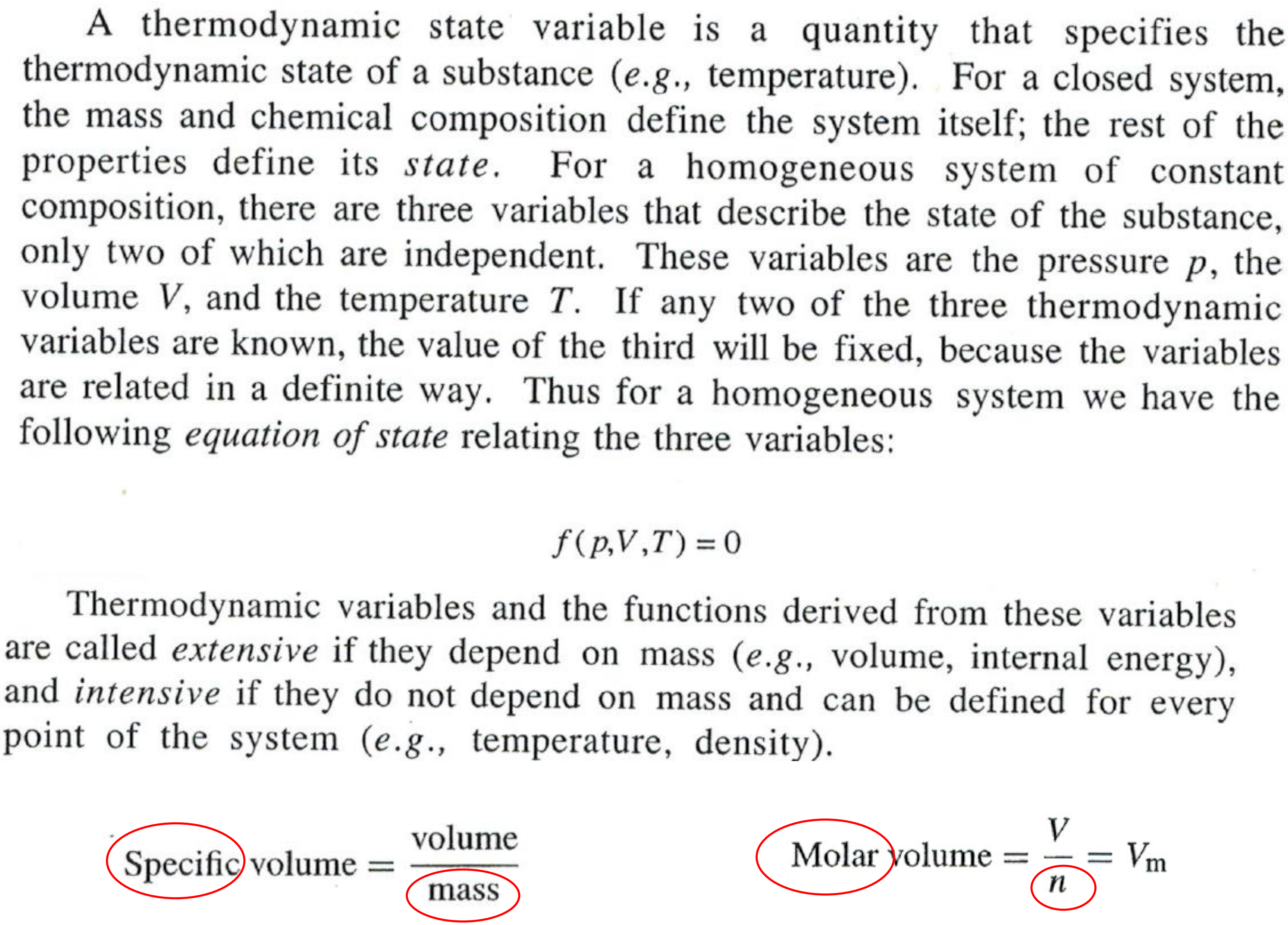
What kinds of mass and energy transfers will be involved? What will be the costs of those transfers? What is the most efficient way to perform the process? Are other processes more efficient?

Basic concepts: examples



Boundary	Process
open	any mass and energy transfer is possible
insulated	adiabatic (no thermal interaction)
rigid	isometric (no volume change)
closed	no bulk or diffusional mass transfer
isolated	no mass or energy interaction

Basic concepts: variables, state



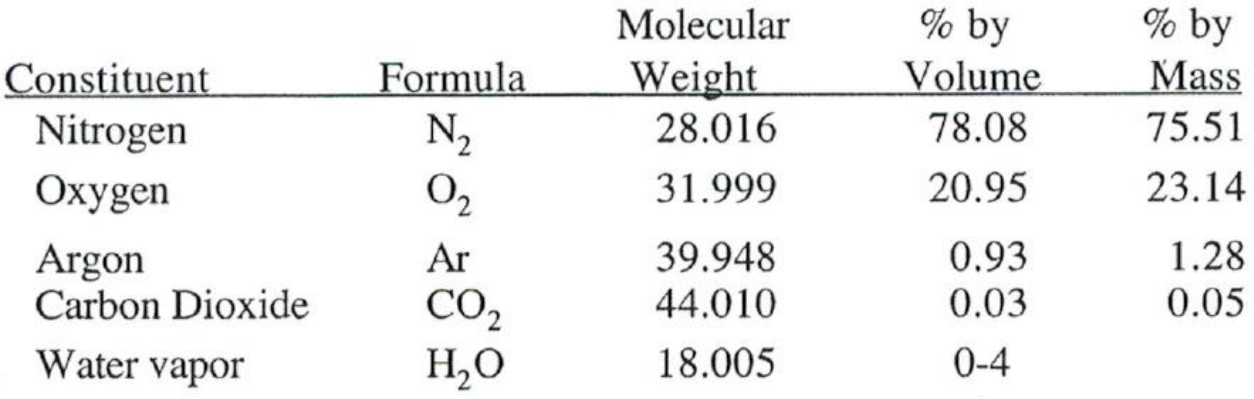
A thermodynamic state variable is a quantity that specifies the thermodynamic state of a substance (*e.g.*, temperature). For a closed system, the mass and chemical composition define the system itself; the rest of the properties define its *state*. For a homogeneous system of constant composition, there are three variables that describe the state of the substance, only two of which are independent. These variables are the pressure p, the volume V, and the temperature T. If any two of the three thermodynamic variables are known, the value of the third will be fixed, because the variables are related in a definite way. Thus for a homogeneous system we have the following *equation of state* relating the three variables:

$$f(p,V,T)=0$$

Thermodynamic variables and the functions derived from these variables are called *extensive* if they depend on mass (*e.g.*, volume, internal energy), and *intensive* if they do not depend on mass and can be defined for every point of the system (*e.g.*, temperature, density).

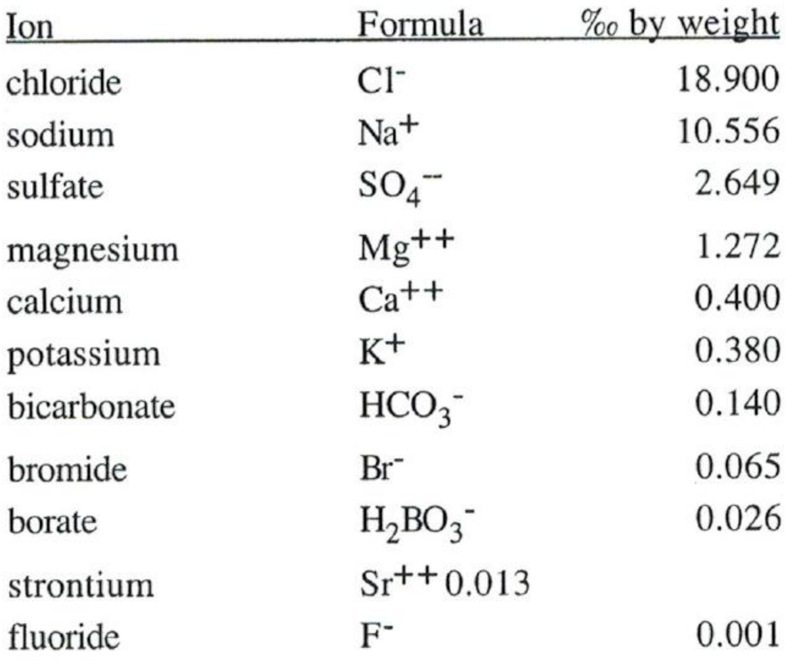
$$\text{Specific volume} = \frac{\text{volume}}{\text{mass}} \qquad \text{Molar volume} = \frac{V}{n} = V_{\mathrm{m}}$$

Composition: Atmosphere &Ocean.



Constituent	Formula	Molecular Weight	% by Volume	% by Mass
Nitrogen	N_2	28.016	78.08	75.51
Oxygen	O_2	31.999	20.95	23.14
Argon	Ar	39.948	0.93	1.28
Carbon Dioxide	CO_2	44.010	0.03	0.05
Water vapor	H_2O	18.005	0-4	

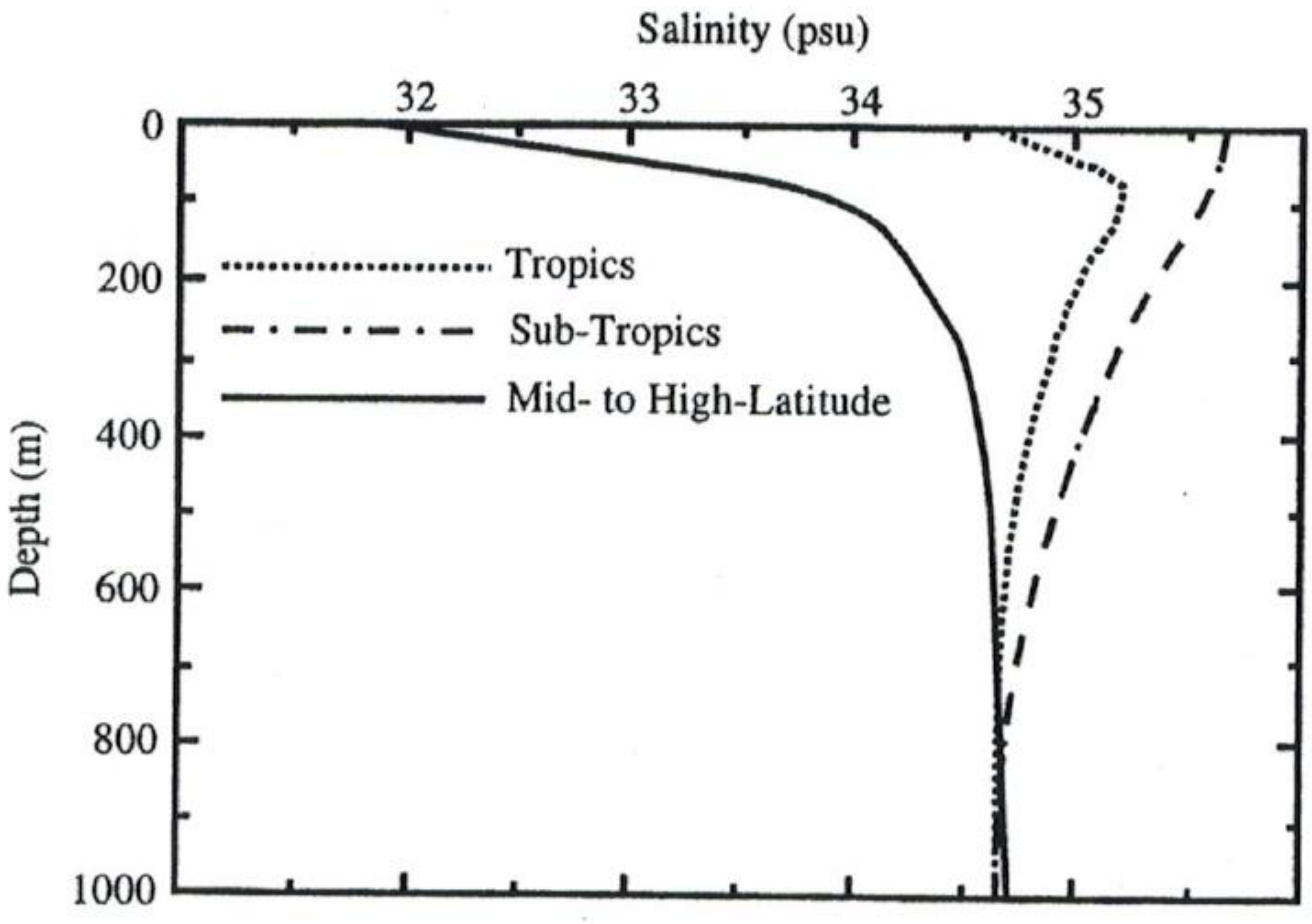
Air (averge) composition



Ion	Formula	‰ by weight
chloride	Cl^-	18.900
sodium	Na^+	10.556
sulfate	SO_4^{--}	2.649
magnesium	Mg^{++}	1.272
calcium	Ca^{++}	0.400
potassium	K^+	0.380
bicarbonate	HCO_3^-	0.140
bromide	Br^-	0.065
borate	$H_2BO_3^-$	0.026
strontium	Sr^{++}	0.013
fluoride	F^-	0.001

Ocean (average) composition

Composition: Oceanic salinity



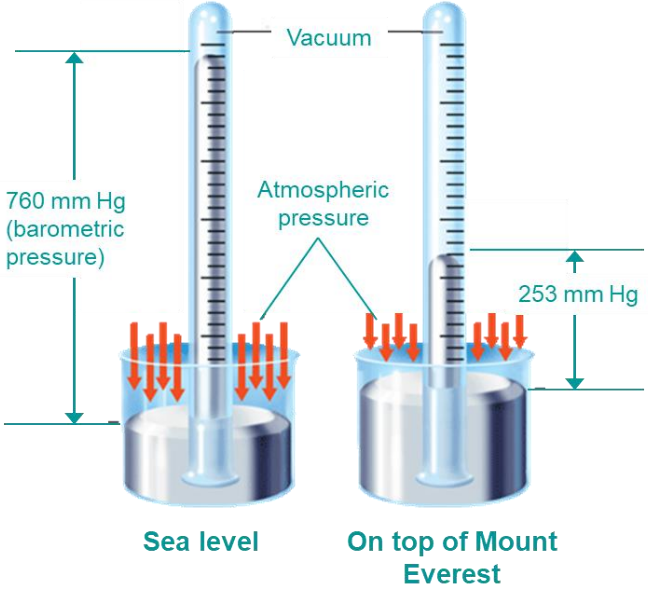
practical salinity unit (psu), which is nearly equivalent to the total mass of dissolved solids in parts per thousand (‰).

Concepts: pressure

Pressure is defined as force per unit area, p = F/A. The pressure at any point in the atmosphere is the weight of air in a column above that point in a unit area. The pressure at any point in the ocean is the sum of the weight of the atmosphere plus the weight of the ocean in a column above the point per unit area. Since the mass of the world ocean is about 270 times the mass of the atmosphere, pressures in the ocean are substantially greater than those in the atmosphere.

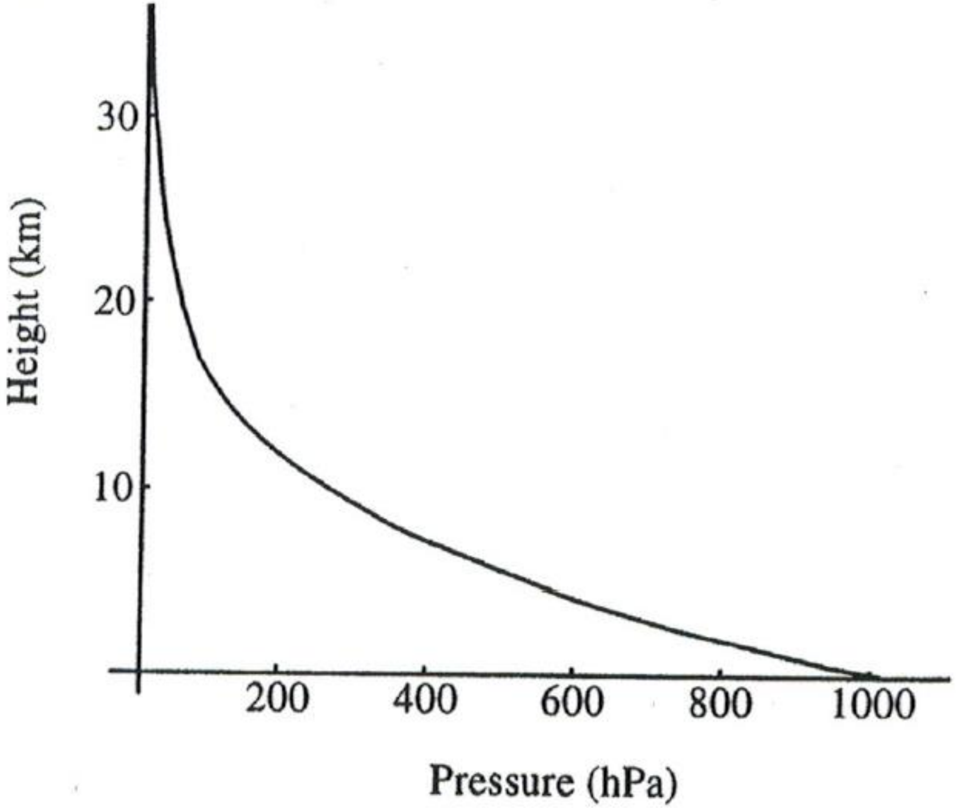
In SI units, the Pascal (Pa) is the unit of pressure, where 1 Pa = 1 N m^{-2}, and N is a Newton. Alternative units of pressure include:

Bar (bar): 1 bar = 10^5 Pa
Millibar (mb): 1 mb = 10^2 Pa
Torricelli (torr): 1 torr = 133.322 Pa
Atmosphere (atm): 1 atm = 1.01325 bar
= 760 torr
= 1.01325 x 10^5 Pa



Concepts: atmospheric pressure

The vertical variation of pressure in the atmosphere is shown in Figure 1.3 to decrease almost exponentially with height, from a mean sea-level pressure of 1013.25 hPa. Approximately 90% of the weight of the atmosphere lies below 15 km.



Concepts: pressure in ocean

The vertical variation of pressure with depth in the ocean is shown in Figure 1.4 to be approximately linear. In dealing with the pressure in the oceans, the atmospheric pressure is subtracted and the pressure at the sea surface is entered as zero. An increase of 10 m in depth in the ocean corresponds to an increase of 10^5 Pa, which is approximately 1 atm. Thus the pressure at a depth of 1 km in the ocean is equivalent to approximately 100 atm.

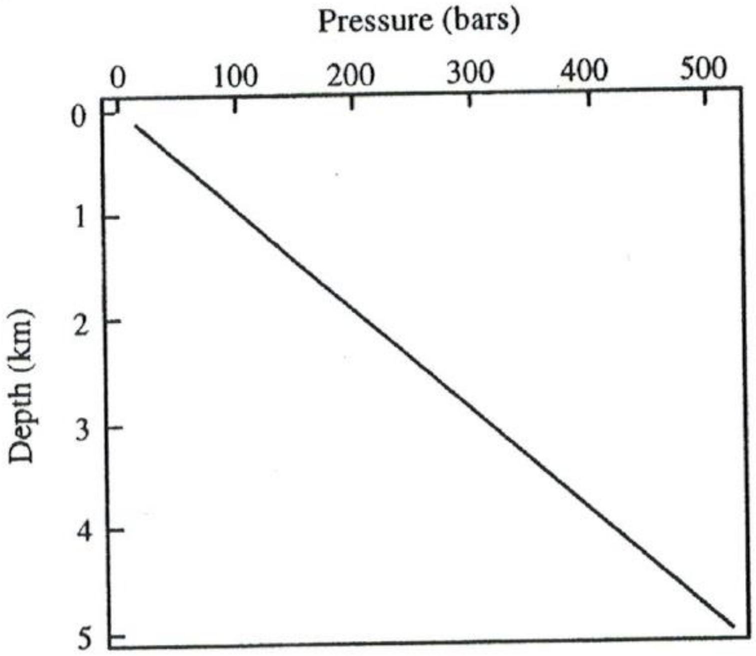


Figure 1.4 Vertical variation of pressure with depth in the ocean.

Concepts: temperature in atmos

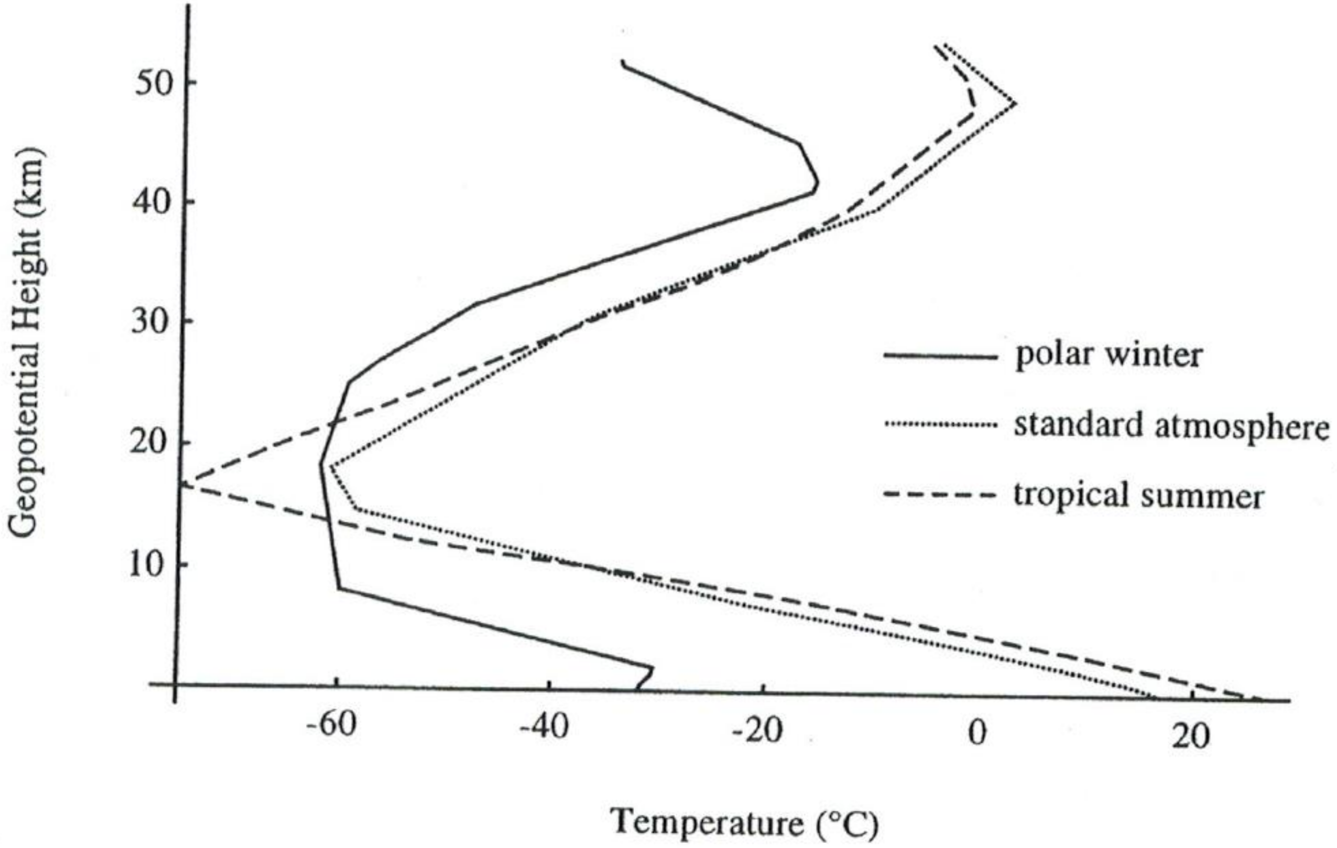


Figure 1.7 Vertical temperature structure in the atmosphere below about 50 km. Temperature decreases with height in the troposphere, except for the polar winter, where surface temperatures are very low, causing a temperature inversion near the surface (U.S. Standard Atmosphere, 1976).

Concepts: temperature in ocean

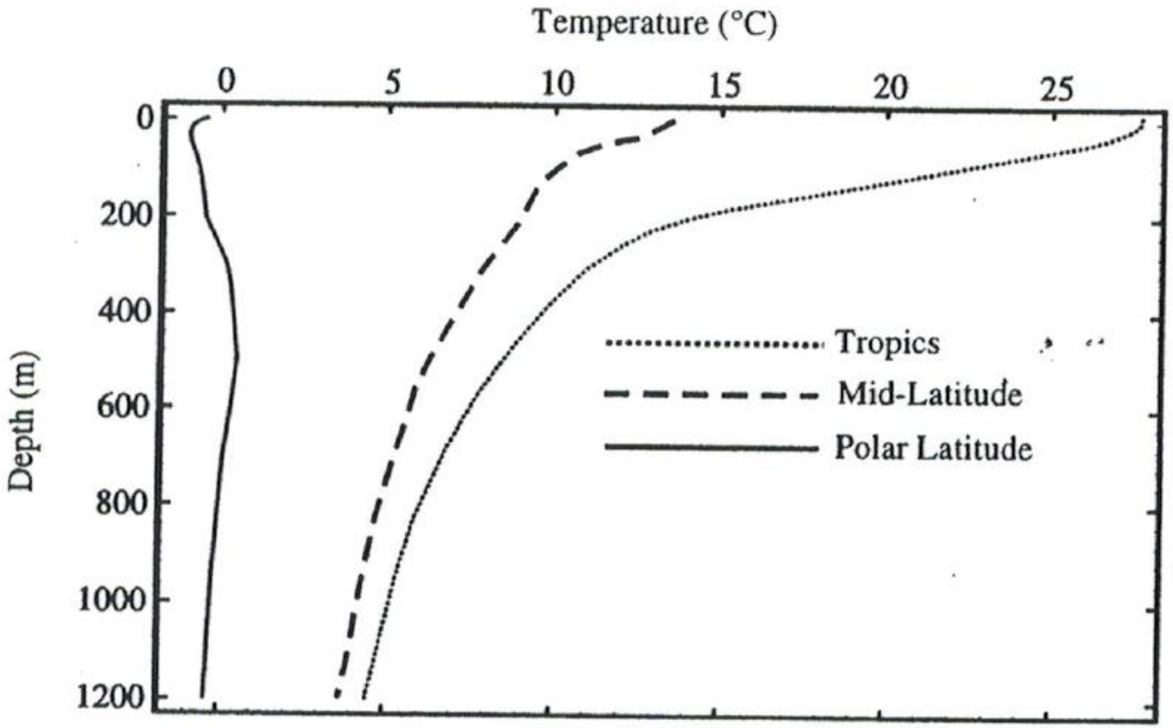


Figure 1.8 Variation of temperature with depth in the upper ocean. The vertical temperature gradient in the upper ocean is largest in the tropics, where surface water is warm. The latitudinal variation of temperature with depth is large in the upper ocean, where surface ~~effects~~ are important. (Data from Levitus, 1982.)

(heating and cooling)

Worksheet time!

Download Worksheet 1 from the Moodle page and work on it.

You might need the PDFs of reading material from the Moodle page as well

Kinetic Theory: Chronology

c.420 BC – atomic theory (Democritus: matter ultimately uncut-able)
1662 – Boyle's law
1738 – Bernoulli *Hydrodynamica* (molecular collisions ➔ gas pressure)
1787 – Charles' law
1798 – atomic theory of heat
1827 – Brownian motion
1834 – ideal gas law
1849 – kinetic theory

microscopic ⇔ macroscopic

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

k = 1.38 x 10^{-23} J K^{-1} (Boltzmann constant)

Equipartitioning of energy: every degree of freedom of a molecule has the same amount of energy (1/2 kT)

Kinetic Theory: Evidence for atoms

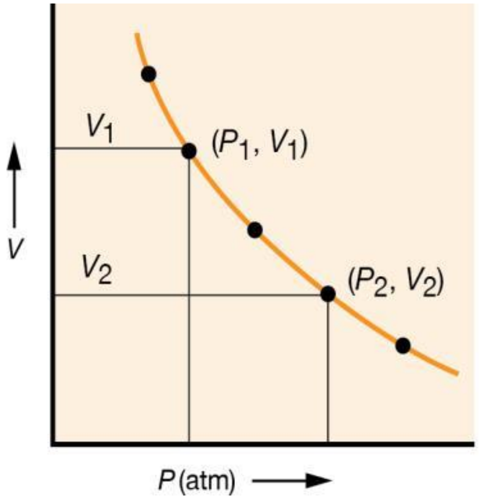
- crystals – regularity of surfaces, cleaving
- mixing different liquids
- change of volume: solid ➔ gas, liquid ➔ gas
- air occupies space and has mass
- Gas laws (Boyle, Dalton, combined ideal gas law)
- diffusion: solid into solid, solid into liquid, gas into gas
- Brownian motion (Einstein proved it).

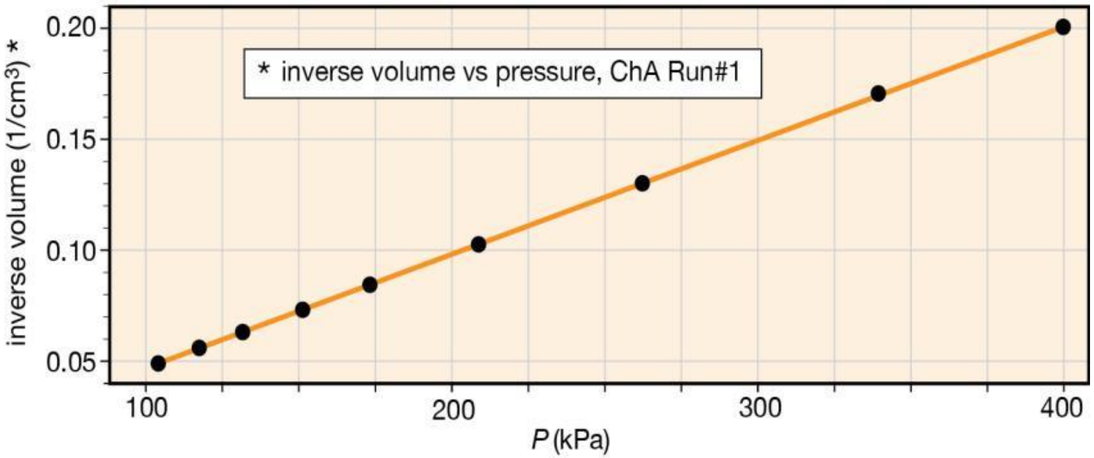
Before Kinetic Theory: gas laws

An empirical law

temperature constant

re-plot to show inverse proportionality





Boyle's law: pV = constant

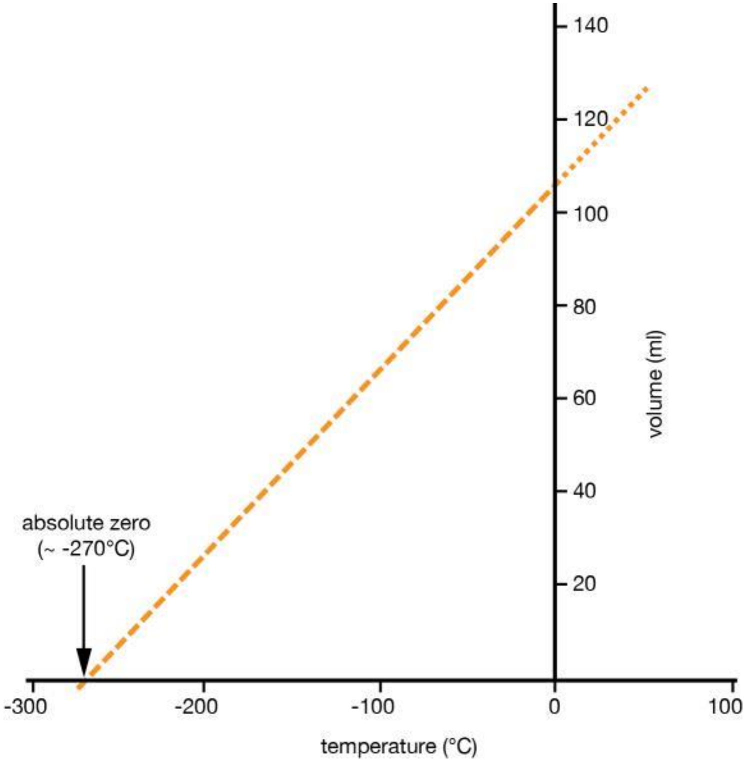
[Clive Sutton (1992) *Words, Science and Learning* Open University Press pp 74-75]

Before Kinetic Theory: gas laws

Another empirical law…

Charles' law: $V \propto T$

In ^{o}C, a linear relationship.
Direct proportionality if T in kelvins,
where K = ^{o}C **+** 273



All relationships combined:

$$\frac{pV}{T} = \text{constant} = nR$$

n # of moles, gas constant R = 8.31 J K^{-1}

The well known ideal gas law!

Kinetic Theory: Misconceptions

Molecules:

- *Do not* have the properties of bulk matter (particles change in size as the temperature changes, particles can melt and solidify)
- *Do not* have air in between them
- *Do not* have thoughts and intentions e.g. ‘they prefer to move to places that are less crowded’.

There is much confusion about the nature of particle motion in solids, liquids and gases.

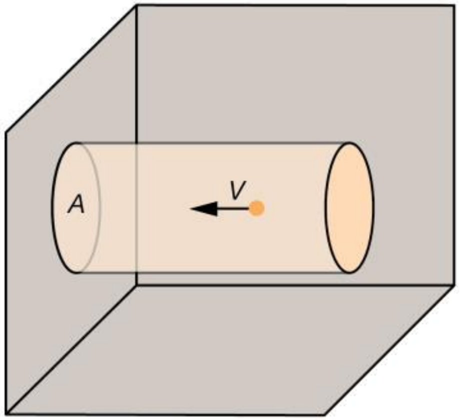
Kinetic Theory: Ideal Gases

Following characteristics:

- huge number of point molecules (occupy negligible volume) in continual random motion (and so ‘kinetic’)
- colliding elastically with each other and with container walls
- no forces between the molecules, except in collision
- time in collisions very small compared to time between collisions
- distance travelled between collisions (‘mean free path’) depends on gas density
- average speed of molecules depends on gas temperature
- in a gas composed of different molecules, the average molecular E_k is the same for all, so those with larger mass have smaller speed

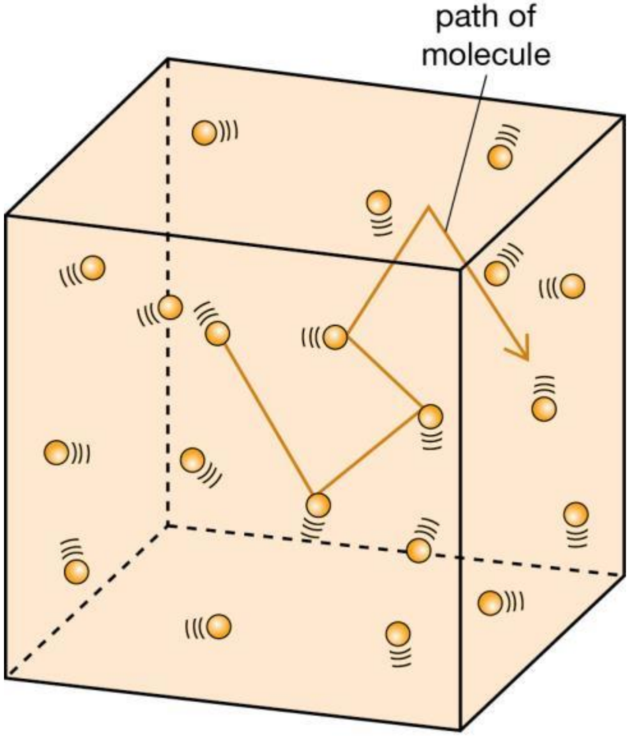
Kinetic Theory: Origin of Gas Pressure

bombardment of the container walls



change of momentum with each collision

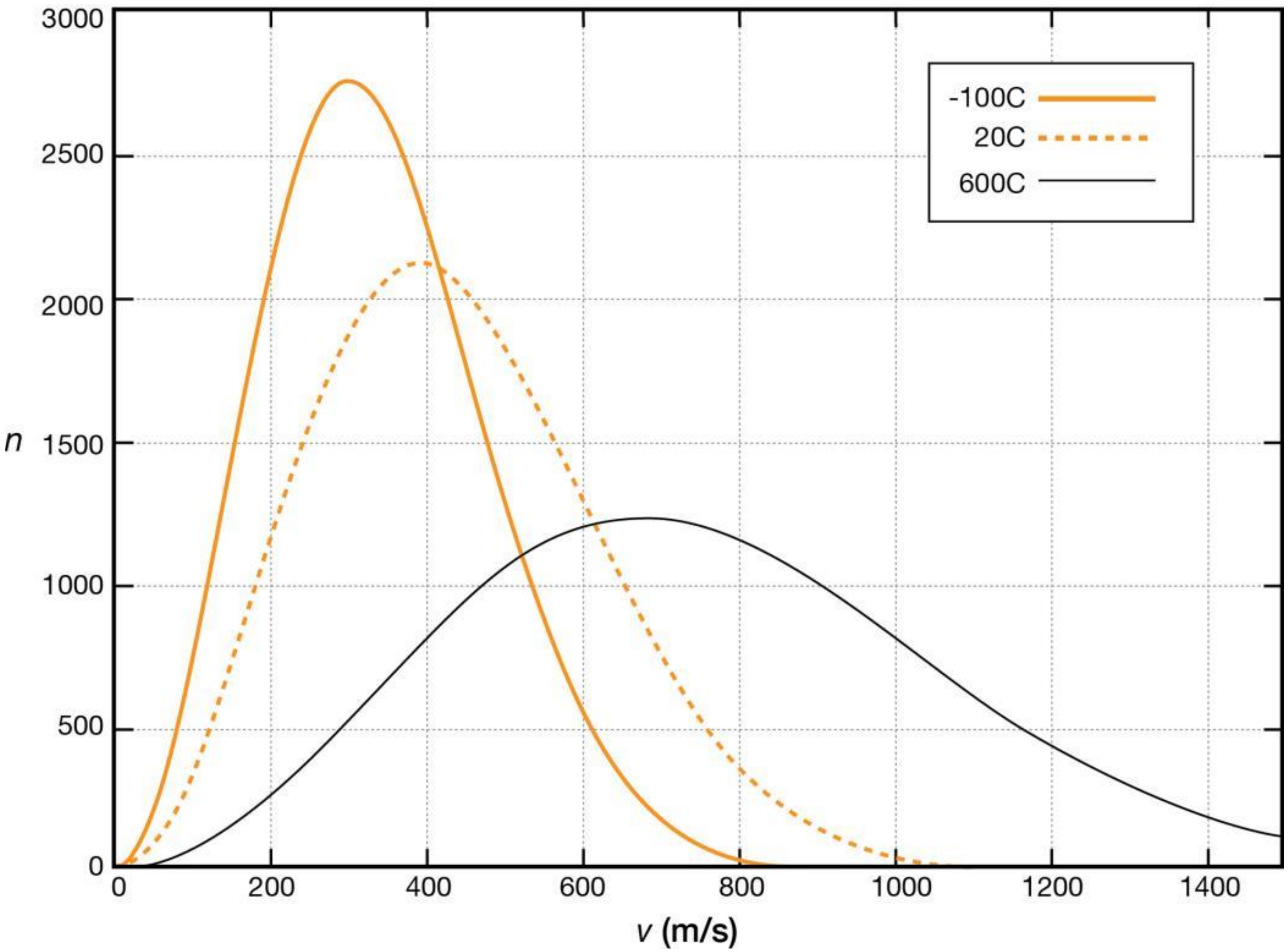
$mv - (-mv) = 2mv$



a gas may be pictured as a collection of widely spaced molecules in continuous, chaotic motion

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{m\Delta v}{\Delta t}$$

Kinetic Theory: Velocity distributions



Distribution of particle speed for 10^6 oxygen particles at -100, 20 and 600 ^{o}C.

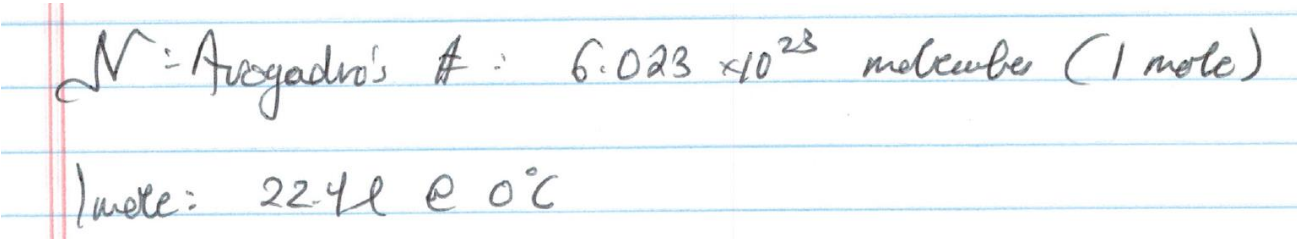
Kinetic Theory: see it in action!

PhET simulation *Gas properties*

Task (spend about 5-10 minutes on these points):

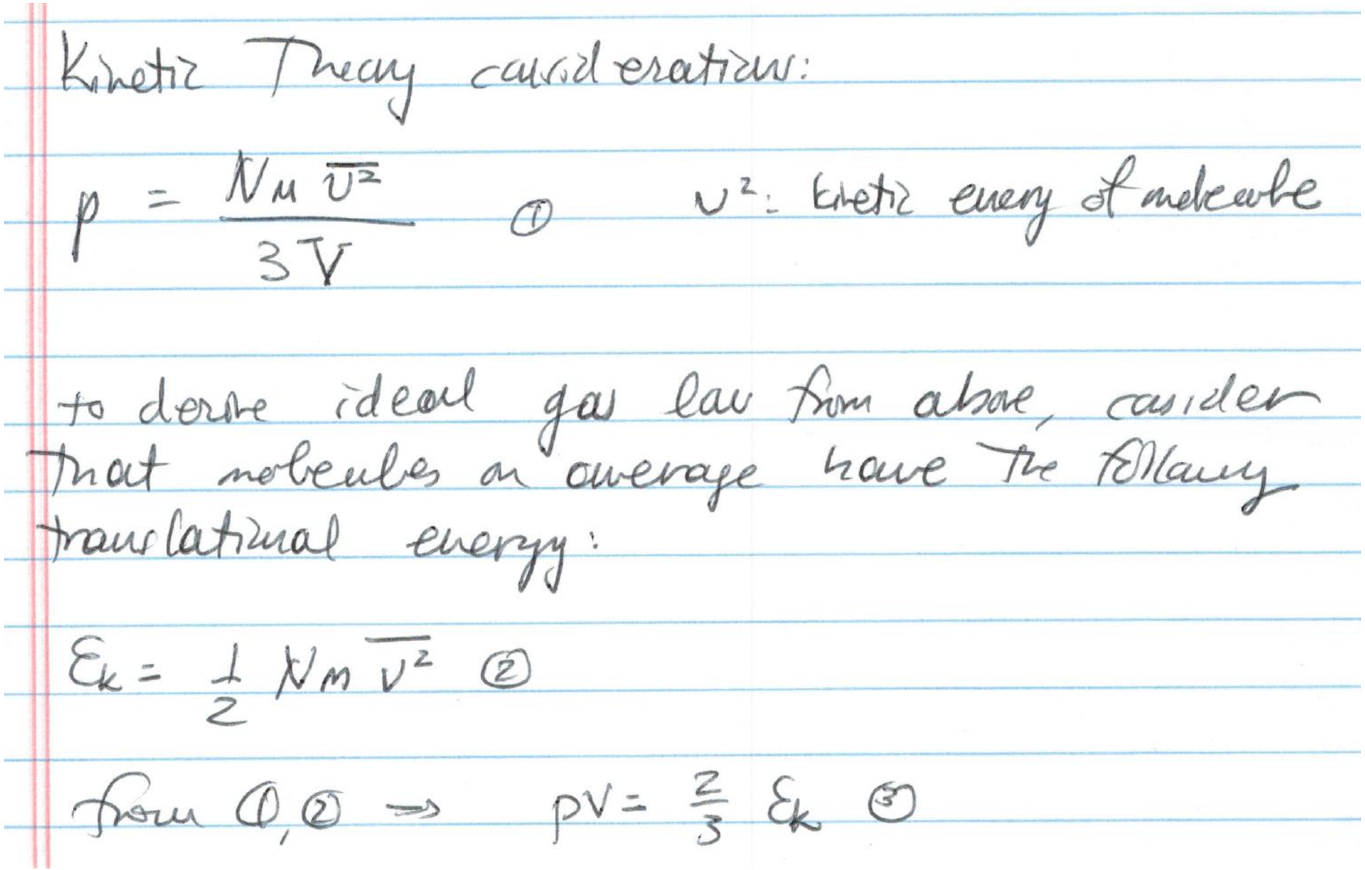
- Pump gas molecules to a box and see what happens as you change the volume, add or remove heat, change gravity, and more.
- Measure temperature and pressure, and discover how the properties of the gas vary in relation to each other.
- Interesting to count number of collisions too and see how they relate to pressure.

Kinetic Theory: gives ideal gas law!



N: Avogadro's #: 6.023×10^{23} molecules (1 mole)

1 mole: 22.4 l @ 0°C



Kinetic Theory considerations:

$$p = \frac{N m \overline{v^2}}{3V} \quad ①$$

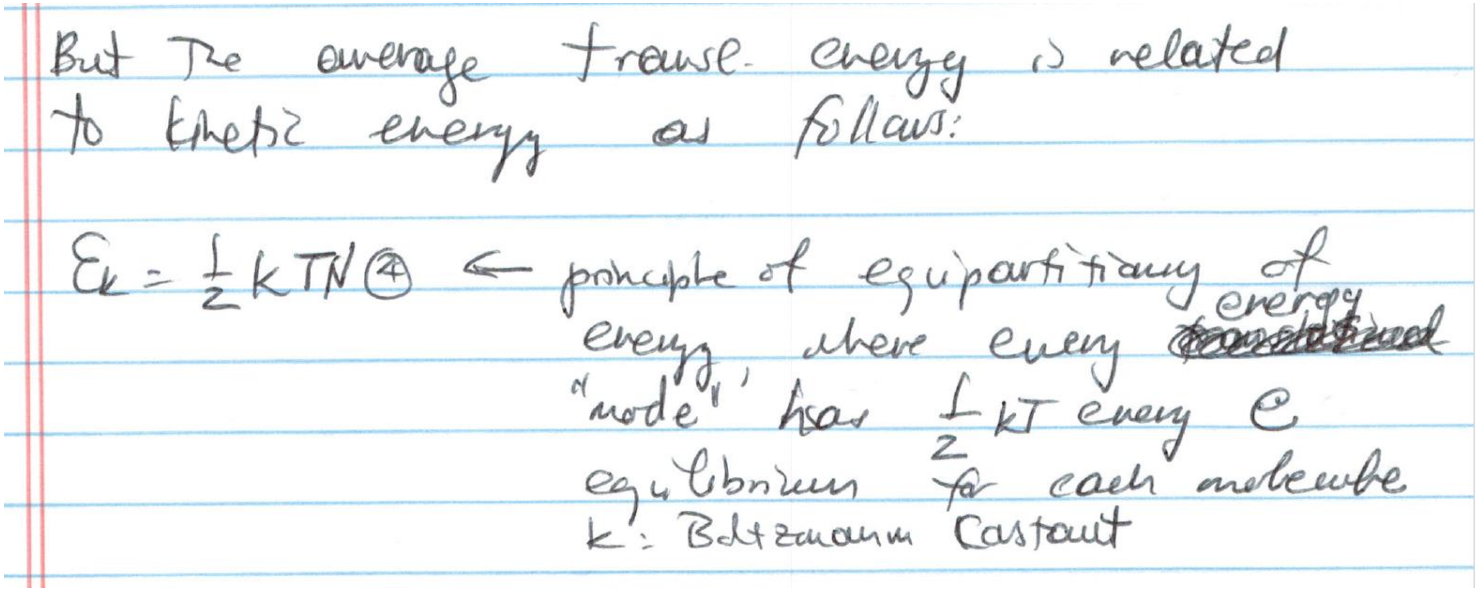
v^2: kinetic energy of molecule

to derive ideal gas law from above, consider that molecules on average have the following translational energy:

$$E_k = \frac{1}{2} N m \overline{v^2} \quad ②$$

from ①, ② $\Rightarrow$ $pV = \frac{2}{3} E_k$ ③

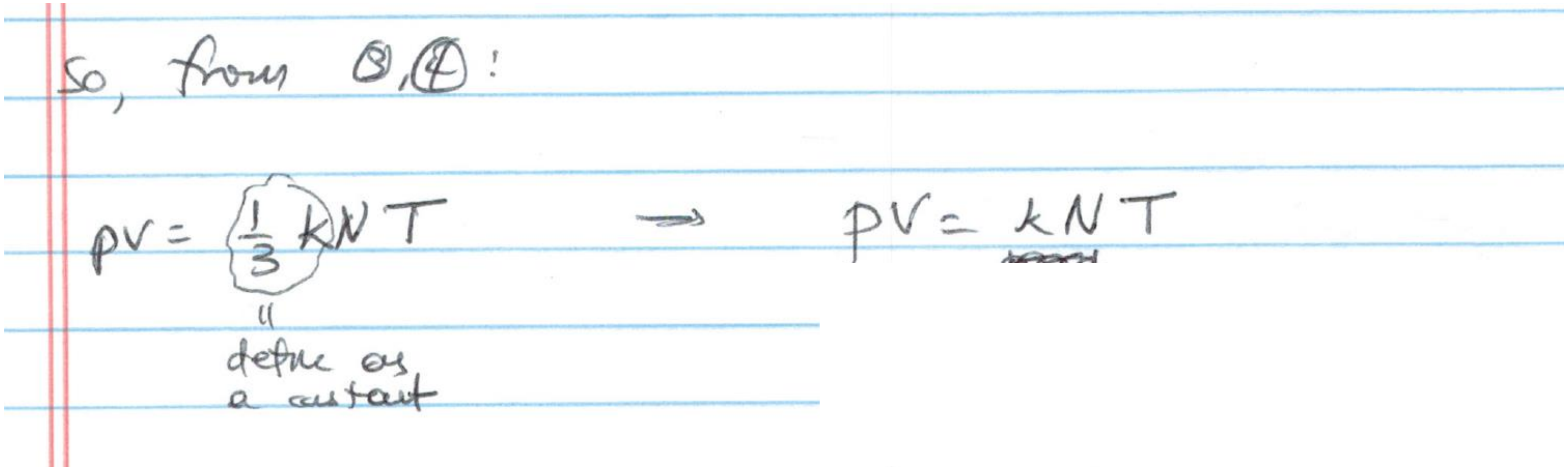
Kinetic Theory: gives ideal gas law!



But the average transv. energy is related to kinetic energy as follows:

$E_k = \frac{1}{2} kTN$ ④ ← principle of equipartition of energy, where every ~~translational~~ energy "mode" has $\frac{1}{2} kT$ energy @ equilibrium for each molecule

k: Boltzmann Constant



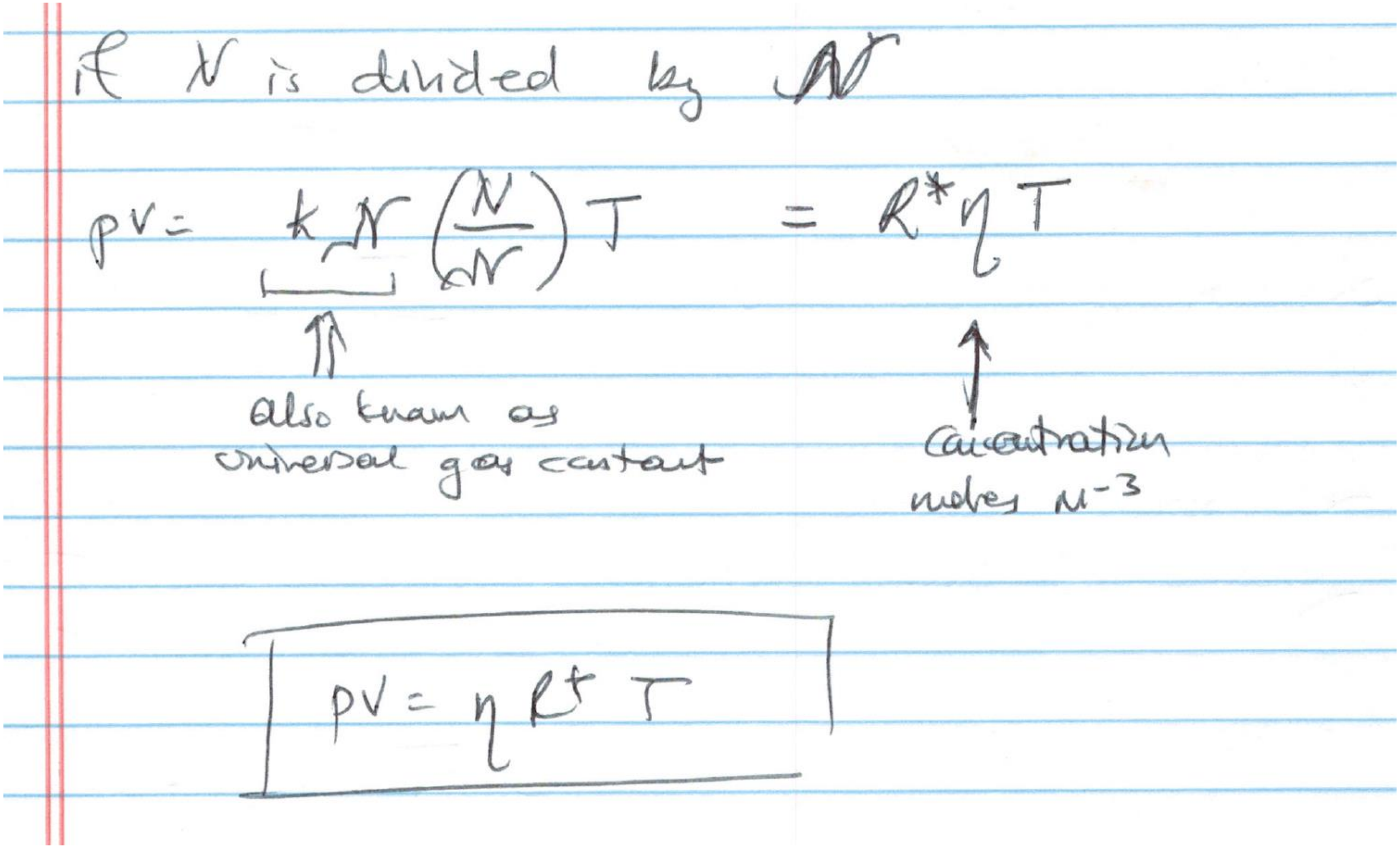
So, from ③,④:

$$pv = \boxed{\frac{1}{3}} kNT \quad \Longrightarrow \quad PV = \underline{k}NT$$

||

define as a constant

Kinetic Theory: gives ideal gas law!



if N is divided by $\mathcal{N}$

$$pv = \underbrace{k\mathcal{N}}_{\Uparrow}\left(\frac{N}{\mathcal{N}}\right)T = R^*\underset{\uparrow}{\eta}\,T$$

also known as universal gas constant

concentration moles m^{-3}

$$\boxed{pv = \eta R^* T}$$

The ideal gas law emerges naturally from kinetic theory