(b) The measurement of pressure

- The pressure of the atmosphere is measured with a barometer.
- The original version of a barometer was invented by Torricelli, a student of Galileo.
- The barometer was an inverted tube of mercury sealed at the upper end.
(b) The measurement of pressure

(a) The pressure exerted by the atmosphere on the surface of mercury in a cup is given by $P = h \rho g$.

It follows that the height of the mercury column is proportional to the external pressure.
(b) The measurement of pressure

- The pressure of a system is measured with a closed-end manometer. The pressure of a system is given by the same equation when a closed-end manometer is used.
Manometers: Closed-end and open-tube

Two versions of a manometer used to measure the pressure of a sample of gas: closed-end and open-tube manometers. (a) The height difference, $h$, of the two columns in the sealed-tube manometer is directly proportional to the pressure of the sample, and $p = h \rho g$, where $\rho$ is the density of the non-volatile viscous liquid.

(b) The difference in heights of the columns in the open-tube manometer is proportional to the difference in pressure between the sample and the atmosphere. In the example shown, the pressure of the sample is $<$ than that of the atmosphere.
Example 1.1 Express one atmosphere pressure in SI units

Calculate the pressure of the earth’s atmosphere at a point where the barometer reads 76 cm (=1 atm) of mercury at 0 °C and the acceleration of gravity is 9.80665 m/s². The density of a mercury at 0 °C is 13.5951 g/cm³, or 13.5951 x 10⁻³ kg/m³

Answer:

Pressure \( P \) is force \( f \) divided by area \( A \): \( P = \frac{f}{A} \)

\[ f = mg = \rho Ahg \quad P = \frac{\rho Ahg}{A} = \rho hg \]

1 atm = 760 mmHg

\[ = (0.76 \text{ m}) \times (13.5951 \times 10^3 \text{ kg/m}^3) \times (9.80665 \text{ m/s}^2) \]

\[ = 101325 \text{ kg-m/s}^2 \cdot \text{m/m}^3 \]

\[ = 101325 \text{ N/m}^2 = 101325 \text{ Pa} = 1.01325 \text{ bar} \]
Exercise Calculating pressure

Suppose Isaac Newton weighed 65 kg. Calculate the pressure he exerted on the ground when wearing (a) boots with soles of total area 250 cm$^2$ in contact with the ground, (b) ice skates, of total area 2.0 cm$^2$.

Answer: The force exerted by Newton is

\[ F = (65 \text{ kg}) \times (9.80665 \text{ m/s}^2) = 6.4 \times 10^2 \text{ N} \]

The force is the same whatever Newton’s footwear.

\[ p = \frac{F}{A} \]

(a) \[ p = \frac{(6.4 \times 10^2 \text{ N})}{(2.50 \times 10^{-2} \text{ m}^2)} = 2.6 \times 10^4 \text{ N m}^2 = 26 \text{ kPa} \]

(b) \[ p = \frac{(6.4 \times 10^2 \text{ N})}{(2.0 \times 10^{-4} \text{ m}^2)} = 3.2 \times 10^6 \text{ N m}^2 = 3.2 \text{ MPa} \]
### Table 1.1 The Pressure units

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pascal</td>
<td>1 Pa</td>
<td>1 N m(^{-2}), 1 kg m(^{-1}) s(^{-2})</td>
</tr>
<tr>
<td>Bar</td>
<td>1 bar</td>
<td>10(^5) Pa</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>1 atm</td>
<td>101325 Pa</td>
</tr>
<tr>
<td>Torr</td>
<td>1 torr</td>
<td>101325/760 Pa</td>
</tr>
<tr>
<td>Millimeter of Hg</td>
<td>1 mmHg</td>
<td>133.322... Pa</td>
</tr>
<tr>
<td>PSI (pound/ in(^2))</td>
<td>1 psi</td>
<td>6.894757 kPa</td>
</tr>
</tbody>
</table>
1.2 The Zeroth Law of Thermodynamics

A commonsense notion of what temperature is?

If two closed systems with fixed volumes are in thermal contact, changes may take place in the properties of both before reaching a state of thermal equilibrium. In this state, the two systems are at the same temperature.
1.2 The Zeroth Law of Thermodynamics

Fig. 1.3

The zeroth law of thermodynamics is concerned with thermal equilibrium between three bodies.

The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with C and if B is in thermal equilibrium with C, then A is in thermal equilibrium with B.
Zeroth Law of Thermodynamics

• Assume that A, B, C each consist of a certain mass of different fluid (a gas or a compressible liquid), then each of the pressure and the volume are independent variables, their intensive states are specified by the pressure AND the volume.

• The macroscopic state of a given mass of fluid of a given composition can be fixed by specifying only the P AND V.

• If a fluid is in thermal equilibrium with another system, it has only one independent variable: pressure OR volume. One or the other can be set arbitrarily, but not both.

• The plot of all the values of P and V for a system in thermal equilibrium with another system is called an isotherm. Each pair of (P,V) on the isotherm corresponds with the same temperature \( \theta \).
Fig 1.4 Isotherms for fluid A

The pressure-volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola (PV = constant) and is called an isotherm.

Boyle’s law: 低壓下對定溫定量的氣體，體積與壓力的乘積為一定值。
1.2 The Zeroth Law of Thermodynamics

**Zeroth Law of Thermodynamics**

- Let’s just state the Zeroth Law of Thermodynamics
  - If bodies $A$ and $B$ are in thermal but not mechanical contact and heat flows from $A$ to $B$ and if $B$ is in thermal contact with $C$ and heat flows from $B$ to $C$ then heat will flow from $A$ to $C$ if they are in thermal contact. In other words,

  \[
  \begin{align*}
  \text{if } \Theta_A &> \Theta_B \quad \text{and} \quad \Theta_B > \Theta_C \quad \Rightarrow \quad \Theta_A > \Theta_C \\
  \text{if } \Theta_A & = \Theta_B \quad \text{and} \quad \Theta_B = \Theta_C \quad \Rightarrow \quad \Theta_A = \Theta_C
  \end{align*}
  \]

**Example:**

- We can call the body $B$ a thermometer and use the zeroth law.
  
- The temperature can be related to $\Theta$, we can just call $T = \Theta$. This can be done rigorously and it defines an absolute zero ($T = 0$).

- Later we may use the entropy, $S$ and internal energy, $U$, of a body to define the temperature.

\[T = \left( \frac{\partial U}{\partial S} \right)_{\text{no work}}\]
1.2 The Zeroth Law of Thermodynamics

Boyle’s Law Isotherm

Straight lines are obtained when the pressure is plotted against $1/V$.

- Boyle’s Law 的一個實例是注射針筒的例子(syringe action): 吸入針筒時, 針筒內的藥水總是看起來比罐子裡的藥水多. 加壓針筒擠出藥水時, 也是因為先降低針筒內的體積, 使內部的壓力大於外壓, 讓藥水流出.

- 另一個實例是CPR 人工呼吸時, 人體肺部與橫隔膜運動的例子:
理想気體狀態方程式 (Ideal gas equation of state)

- Charles 與 Gay-Lussac 發現在定壓下，氣體的體積與溫度成正比。\[ V = V_0 (1 + \alpha T); \quad \alpha = 1/273.15 \]

- 溫度的單位為 1 Kelvin (1 K), for triplet point of water: \( T = 273.16 \text{ K} \) and \( P = 611 \text{ Pa} \)

- 對兩個溫度下PV乘積可表示為: \( \frac{P_2 V_2}{P_1 V_1} = \phi(\theta_1, \theta_2) \)

- 以PV乘積的比值定義的溫標比,可表示為: \( \frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1} \)

- 對定量氣體, 莫耳體積為內涵變數,理想気體狀態方程式可表示為:
  \[
  \frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} = R
  \]
### Real vs. Ideal Gas Behavior

- **For the Volume Pressure relationship (i.e.: Boyle's Law):**
  
  \( n_1 = n_2 \) and \( T_1 = T_2 \) therefore the \( n \)'s and \( T \)'s cancel in the above expression resulting in the following simplification:

  \[ P_1 V_1 = P_2 V_2 \]  
  (mathematical expression of Boyle's Law)

- **For the Volume Temperature relationship (i.e.: Charles’s Law):**
  
  \( n_1 = n_2 \) and \( P_1 = P_2 \) therefore the \( n \)'s and the \( P \)'s cancel in the original expression resulting in the following simplification:

  \[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]  
  (mathematical expression of Charles's Law)

- **For the Pressure Temperature Relationship (i.e.: Gay-Lussac's Law):**
  
  \( n_1 = n_2 \) and \( V_1 = V_2 \) therefore the \( n \)'s and the \( V \)'s cancel in the above original expression:

  \[ \frac{P_1}{T_1} = \frac{P_2}{T_2} \]  
  (math expression of Gay-Lussac's Law)

- **For the Volume mole relationship (Avagadro's Law):**
  
  \( P_1 = P_2 \) and \( T_1 = T_2 \) therefore the \( P \)'s and \( T \)'s cancel in the above original expression:

  \[ \frac{V_1}{n_1} = \frac{V_2}{n_2} \]  
  (math expression for Avagadro's Law)
Fig. 1.5 Plot of molar volume vs. T for a given amount of a real gas at two low pressure $p_1$ and $p_2$, as given by Gay-Lussac’s law:

$$V = V_0 \left(1 + \Delta T\right); \quad \Delta = 1/273.15$$

Note that in each case they extrapolate to zero volume at -273.15 $°$ C.

Celsius scale $t$ is formally defined by:

$$t/ °C = T/K - 273.15$$
1.3 The Ideal Gas Temperature Scale

- Plot of the volume of a gas as a function of temperature at constant pressure. Lines of constant pressure are known as isobars; notice how an infinitely small V implies a temperature near -273 °C. The volume of a gas should extrapolate to zero near -273 °C.

- Charles's Law的一个实例就是热气球。在填充加热空气后，热空气膨胀填满气球内部，气球体积变大，取代较多的外部冷空气，在不同比重的介质中，获得浮力以抵销其重力，使气球可以昇空。事实上第一个氢气球就是查理在1783年建造，且飘上昇约3000公尺。
Pressure vs. T

• The pressure also varies linearly with the temperature, and extrapolates to zero at

\( T = 0 \) (or -273.15 \( ^\circ C \))

• Lines of constant volume are known as isochors (等體積線). Pressure falls to zero as \( T \) approaches absolute zero (i.e., no molecular motion).

Based on the second law of thermodynamics or statistical mechanics, the ideal temperature scale is independent of the properties of any substance.
• 1954年,第十屆國際計量大會決定，選取純水的三相點(冰、水、水蒸汽三相平衡共存時的溫度)作為一個固定參考點，規定其溫度為273.16K。在純水三相點上，由實驗測出理想氣體的$\rho V_m$值，依 $\rho V_m = AT$ 可決定出常數A之值為氣體常數R，實驗結果是 $A = R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$ (此值是基於在氬氣中的聲速值推得).

• Temperature unit in 1 Kelvin (1 K):
  - 水的三相點 (triplet point): $T = 273.16 \text{ K}$ and $P = 611 \text{ Pa}$.
  - 水的凝固點 (freezing point): $T = 273.15 \text{ K}$ and $P = 101325 \text{ Pa}$.
  - 水的沸點 (boiling point): $T = 373.12 \text{ K}$ and $P = 101325 \text{ Pa}$.

• Celsius scale ($t$, °C): $t/\degree\text{C} = T/K - 273.15$

• ‘The Ideal Gas Temperature Scale’ is defined by: $T = \lim_{p\to0} \left( \frac{P\bar{V}}{R} \right)$

• The proportionality constant is called the gas constant R
1.3 The Ideal Gas Temperature Scale

理想氣體常數 (Ideal gas constant, R)

\[ R = \frac{PV}{T} \]

- \( R = 0.0820667 \text{ L-atm/K-mol} \)
- \( R = 0.0831451 \text{ L-bar/K-mol} \)
- \( R = 8.31451 \text{ J/K-mol} \)
- \( R = 1.98722 \text{ cal/K-mol} \)
Example 1.2 Express the gas constant in various units

Calculate the value of \( R \) in cal K\(^{-1}\) mol\(^{-1}\), L bar K\(^{-1}\)mol\(^{-1}\), and L atm K\(^{-1}\)mol\(^{-1}\)

**Answer:**
- Since the calorie is defined as 4.184 J
  \[ R = \frac{8.31451 \text{ J K}^{-1} \text{ mol}^{-1}}{4.184 \text{ J/cal}} = 1.98722 \text{ cal K}^{-1} \text{ mol}^{-1} \]
- Since the liter is 10\(^{-3}\) m\(^3\) and the bar is 10\(^5\) Pa
  \[ R = \frac{8.31451 \text{ Pa m}^3 / \text{K}^{-1} \text{mol}^{-1}}{10^3 \text{ L/m}^3} \times \frac{10^{-5} \text{ bar/Pa}}{1} \]
  \[ = 0.0831451 \text{ L bar K}^{-1} \text{ mol}^{-1} \]
- Since the atm is 1.01325 bar
  \[ R = \frac{0.0831451 \text{ L bar K}^{-1} \text{ mol}^{-1}}{1.01325 \text{ bar/atm}} \]
  \[ = 0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1} \]
Molar mass:

- A mole $n$: the amount of substance that has as many atoms or molecules as 0.012 kg of $^{12}$C. due to the molecular interaction forces.

- **Molar mass** $M$: the mass divided by the amount of substance $n$, its SI unit is kg mol$^{-1}$

- The molar mass $M$ is related to the molecular mass $m$ by $M = N_A m$, where $N_A$ is the *Avogadro constant* and $m$ is the mass of a single molecule.

- $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$ based on the measurements of the speed of sound in argon.
Exercise

The density of a noble gas was found to be 1.23 g/L at 330 K and 25.5 kPa. What is the molar mass of the compound?

Answer:

\[
p = \frac{nRT}{V} = \frac{mRT}{MV} = \frac{\rho RT}{M}
\]

\[M \text{ (molar mass)}\]

\[= (1.23 \text{ g/L} \times 10^{-3} \text{ kg/g} \times 10^3 \text{ L/m}^3) \times (8.3145 \text{ J/K-mol}) \times (330 \text{ K}) / (25.5 \times 10^3 \text{ N/m}^2 )\]

\[= 0.132 \text{ kg/mol}\]
John Dalton (1766–1844) studied the effect of gases in a mixture. He observed that the total pressure $P_{\text{total}}$ of a gas mixture was the sum of the partial pressure ($P_i$) of each gas $i$, 

$$P_{\text{total}} = P_1 + P_2 + P_3 + \ldots + P_n$$

- The partial pressure is defined as the pressure of a single gas in the mixture as if that gas alone occupied the container.
PV = nRT applies to a mixture of ideal gases.

Total amount of gas $n = n_1 + n_2 + n_3 + \ldots$

$$P = (n_1 + n_2 + n_3 + \ldots) \frac{RT}{V}$$

$$= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V} + \ldots$$

$$= P_1 + P_2 + P_3 + \ldots = \sum P_i$$

$P_i = n_i \frac{RT}{V}$: partial pressure of species $i$

$P_i = n_i \frac{RT}{V} = n_i \frac{P}{n} = \frac{n_i}{n} P = y_i P$

$y_i$: mole fraction of $i$; $y_i = \frac{n_i}{n}$; also $\sum y_i = 1$

In binary mixture of ideal gases;

$$P_1 = y_1 P = (1 - y_2) P$$

$$P_2 = y_2 P$$

$$P_1 + P_2 = (1 - y_2) P + y_2 P = P$$
The total pressure $p$ and partial pressures $p_A$ and $p_B$ of components of a binary mixture of gases as the composition changes from pure A to pure B. The sum of the partial pressures is equal to the total pressure. If the gases are perfect, then the partial pressure is also the pressure that each gas would exert if it were present alone in the container.
There are really two ways of determining the Partial Pressure of a Gas:

1. Using the Ideal Gas Law Equation.
2. Using the Mole Fraction Relation.

If one has the quantity of each gas either in moles or grams in the mixture, the volume, and the temperature of the gas mixture, then one can find the Partial Pressure of each gas:

**Exercise:**

If we have 2 moles of H₂, 4 moles of O₂, and 6 moles of He in a 5 liter vessel at 27 °C, determine the Partial Pressure of each gas and the Total Pressure of the mixture.
Real vs. Ideal Gas Behavior

- Using the Ideal Gas Law Equation:
  1. Convert the temperature to Kelvin: \( K = 27 + 273 = 300 \text{ K} \)
  2. Using the \( PV = nRT \) equation determine \( P \) for \( \text{H}_2 \):
     \[
     P_{\text{H}_2} = \frac{(2 \text{ mol H}_2)(0.0821 \text{ liter-atm/K-mol})(300 \text{ K})}{5 \text{ liters}} = 9.85 \text{ atm}
     \]
  3. Determine the Partial Pressure for the \( \text{O}_2 \):
     \[
     P_{\text{O}_2} = \frac{(4 \text{ mol O}_2)(0.0821 \text{ liter-atm/K-mol})(300 \text{ K})}{5 \text{ liters}} = 19.7 \text{ atm}.
     \]
  4. Determine the Partial Pressure of \( \text{He} \):
     \[
     P_{\text{He}} = \frac{(6 \text{ mol He})(0.0821 \text{ liter-atm/K-mol})(300 \text{ K})}{5 \text{ liters}} = 29.55 \text{ atm}
     \]

Total Pressure \( P = P_{\text{H}_2} + P_{\text{O}_2} + P_{\text{He}} = 9.85 + 19.7 + 29.55 = 59.1 \text{ atm} \)
Using the Mole Fraction Relationship

1. If one knows the moles or grams of each gas and the total pressure, one can determine the Partial pressure of each gas with the following formula:

\[ P_1 = y_1 \times (P_{\text{total}}) \]

where \( y_1 \) = mole fraction of the gas

2. Mole Fraction is defined as the moles of the gas divided by the total moles of all the gases in the mixture:

\[ \text{Mole Fraction of Gas 1} = \frac{\text{Moles of Gas 1}}{\text{Total Moles}} \]

Determine the Partial Pressure of each gas in a mixture made up of 6 grams of H\(_2\), 32 grams O\(_2\), and 56 grams of N\(_2\) if the total Barometric Pressure is 750 torr?
Example 1.3 Calculation of partial pressure

A mixture of 1 mol of methane and 3 mol of ethane is held at a pressure of 10 bar. What are the mole fractions and partial pressure of the two gases?

Answer: The mole fraction of methane:

\[ y_m = \frac{1}{4} = 0.25 \]
\[ P_m = y_m P = (0.25) (10 \text{ bar}) = 2.5 \text{ bar} \]

The mole fraction of ethane:

\[ y_e = \frac{3}{4} = 0.75 \]
\[ P_e = y_e P = (0.75) (10 \text{ bar}) = 7.5 \text{ bar} \]
Example 1.4 Express relative humidity as mole fraction of water

Partial pressure of water vapor in air at equilibrium at 20 ℃ with relative humidity of 50% (maximum humidity is 2330 Pa). If P = 1 bar, what is the mole fraction of water in the air?

Answer: Assume the gas mixture behaves as an ideal gas.

\[
y_{H_2O} = \frac{P_i}{P} = \frac{(0.5) (2330 \text{ Pa})}{10^5 \text{ Pa}} = 0.0117
\]
Real vs. Ideal Gas Behavior

Real Gases:
- due to the molecular interaction forces.
- imperfect behavior at high p or low T,
- or when close to the condensation point,

• In real gas, "intermolecular forces" would be present that would cause gas molecules to be interdependent instead of independent of one another?
  - Intermolecular forces are electrical forces that exist between molecules that would cause one molecule to influence another. Such forces will cause a gas to deviate from Ideal Gas behavior.
  - Intermolecular forces are called Van Der Waals forces.
• Johannes Diderik van der Waals (1837-1923), a Dutch physicist, won the 1910 Nobel Prize in Physics for his work on the equation of state for gases and liquids. This is an semiempirical theory, which means it is based upon experimental observations, combined with a rigorous thermodynamic treatment.
- There are three such types of Van Der Waals forces:

1. **London Dispersion Forces** which are forces that exist between molecules as a result of positive nuclei of one molecule attracting the electrons of another molecule. All molecular substances exhibit London Forces which are the weakest of the Van Der Waals forces.

2. **Dipole-Dipole interactions** which are forces that exist between polar molecules where the positive end of one molecule attracts the negative end of another molecule. Only polar molecules can exhibit this type of Van Der Waals forces and is considered the second strongest.

3. **Hydrogen bonding interactions** are forces that exist between molecules that have a hydrogen atom bonded to a highly electronegative atom such as Oxygen, Nitrogen, or Fluorine. This represent a strong dipole that will have the Hydrogen end (positive) attracting the negative end (O,N, or F) of other molecules. This type of Van Der Waals force represents the strongest type.
Attractive forces:
- assist compression of gas
- can have influence over a long distance (close but not touching)
- operative at moderate pressures.

Repulsive forces:
- assist expansion of gas
- significant when molecules are close to one another
- operative at high pressures, when intermolecular distances are near a single molecular diameter
Potential Energy

The variation of the potential energy $U$ of two molecules on their separation $r$. The intermolecular Force $= \left( \frac{\partial U}{\partial r} \right)$

High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.
1.5 Real Gases and the Virial Equation

Compression factor: $Z$

The compression factor of a gas can be defined as a ratio of real & ideal molar volumes: $Z = \frac{V_m \text{ [real]}}{V_m \text{ [ideal]}}$

where $V_m$ the molar volume: $V_m = \frac{V}{n}$.

$V_m \text{ [ideal]} = \frac{RT}{p}$

$V_m \text{ [real]} = V_m \text{ [ideal]} + b = \frac{RT}{p} + b$

$Z = \frac{V_m \text{ [real]}}{V_m \text{ [ideal]}}$

$= \frac{p V_m \text{ [real]}}{RT}$

$= 1 + b \left( \frac{p}{RT} \right)$

$= 1 + \frac{b}{V_m \text{ [ideal]}}$

• For ideal gas, $V_m \text{ [real]} = V_m \text{ [ideal]}$; or $Z = 1$.

• Departure from $Z=1$ means that a gas is not behaving as an ideal gas.
1.5 Real Gases and the Virial Equation

Molecular interaction forces:

- At high pressure, \((pV_m > RT, \text{ or } Z > 1)\); molecules almost in contact, the short range repulsive force make volume expansion more difficult to compress than perfect gas.

- At intermediate pressure, \((pV_m < RT, \text{ or } Z < 1)\); molecules separated in several molecular diameter, the long range attractive force overcome the repulsive force, make volume contraction easier to favor compression than perfect gas.

- At very low pressure, \((pV_m \sim RT, \text{ or } Z \sim 1)\); molecules occupy a large volume, far apart from each other; both forces ineffective nearly perfectly.
1.5 Real Gases and the Virial Equation

**Fig. 1.7 Compressibility factor Z**

Influence of high pressure on the compressibility factor, \( Z = \frac{PV_m}{RT} \), for \( N_2 \) and \( O_2 \) at 298 K.
1.5 Real Gases and the Virial Equation

Fig. 1.8 Compressibility factor $Z$

Influence of pressure on the compressibility factor, $Z = \frac{PV_m}{RT}$ for nitrogen at different temperature (given in °C)
- From the molecular view, we could say that the lowering of the pressure allowed the gas molecules to spread farther out from one another. Since the molecules are farther apart, there were fewer intermolecular forces acting upon them and the intermolecular forces are approaching zero. (At zero intermolecular forces the gas would behave as an ideal gas).

- Raising the temperature of the gas sample in the lab would increase the Average Kinetic Energy of the gas molecules and cause them to speed up in their motion to one another. This increase in speed will overcome any intermolecular forces acting between the molecules and the gas would behave more as an ideal gas.