Evaluation of properties

Part I

Pressure

- Let us begin by considering a small area *A* passing through a point in a fluid at rest. The fluid on one side of the area exerts a compressive force on it that is normal to the area, F_{normal}
- An equal but oppositely directed force is exerted on the area by the fluid on the other side. For a fluid at rest, no other forces than these act on the area. The pressure p at the specified point is defined as:

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

Pressure

- In an elemental way, **pressure is defined as force divided by the area to which the force is applied**.
- From a microscopic point of view, the origin of the **force exerted** by a gas is the incessant battering of the molecules **on the walls of its container**.
- The **collisions are so numerous** that they exert an effectively steady force, which is experienced as a **steady pressure**.
- The pressure of a gas is therefore an indication of whether a container that contains the gas will be in **mechanical equilibrium** with another gas with which it shares a movable wall.

Pressure Units

The SI unit of pressure and stress is the *pascal*, *Pa*, where

$$1\ pascal = 1\ N/m^2.$$

However, it is convenient to work with multiples of the *pascal*:

$$1\ kPa = 10^3\ N/m^2$$

$$1\ bar = 10^5\ N/m^2$$

$$1\ MPa = 10^6\ N/m^2$$

Pressure Units

- Although **atmospheric pressure varies with location on the earth**, a standard reference value can be defined and used to express other pressures.

- 1 standard atmosphere (atm) = 1.01325 x 10^5 N/m^2

- 1 bar = 10^5 Pa

- A pressure of **1 bar** is the **standard pressure** for reporting data.

Pressure Measurement

- Pressure as discussed above is called absolute pressure.
- Although absolute pressures must be used in thermodynamic relations, pressure-measuring devices often indicate the difference between the absolute pressure in a system and the absolute pressure of the atmosphere existing outside the measuring device.
- The magnitude of the difference is called a gage pressure or a vacuum pressure.

Pressure Measurement

- The term **gage pressure** is applied when the pressure in the system is greater than the local atmospheric pressure, p_{atm}:

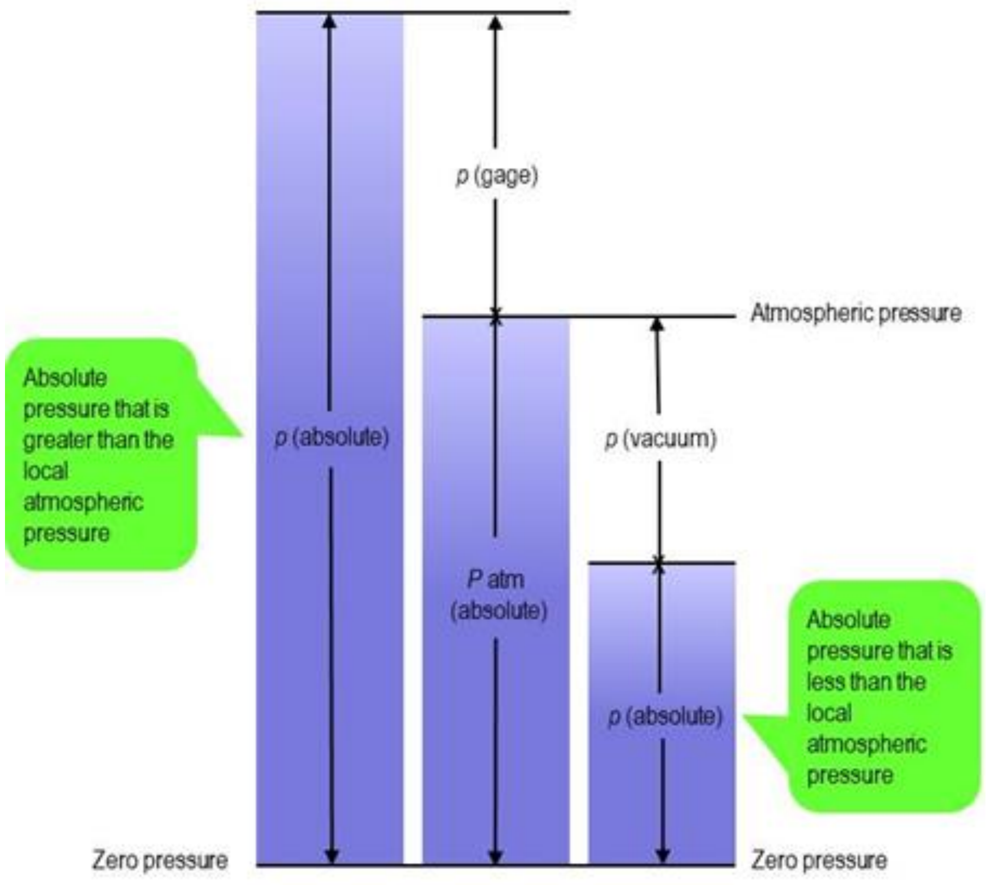
$$p(\text{gage}) = p(\text{absolute}) - p_{atm}\ (\text{absolute})$$

- When the local atmospheric pressure is greater than the pressure in the system, the term **vacuum pressure** is used:

$$p(\text{vacuum}) = p(\text{absolute}) - p_{atm}\ (\text{absolute})$$

Pressure Measurement

Relationships among the absolute, atmospheric, gage, and vacuum pressures.



Pressure Measurement

- The pressure exerted by the atmosphere is measured with a **barometer**. The original version of a barometer was an inverted tube of mercury sealed at the upper end.

- When the **column of mercury** is in mechanical equilibrium with the atmosphere, the pressure at its base is equal to that exerted by the atmosphere.

- It follows that the **height of the mercury column is proportional to the external pressure**.

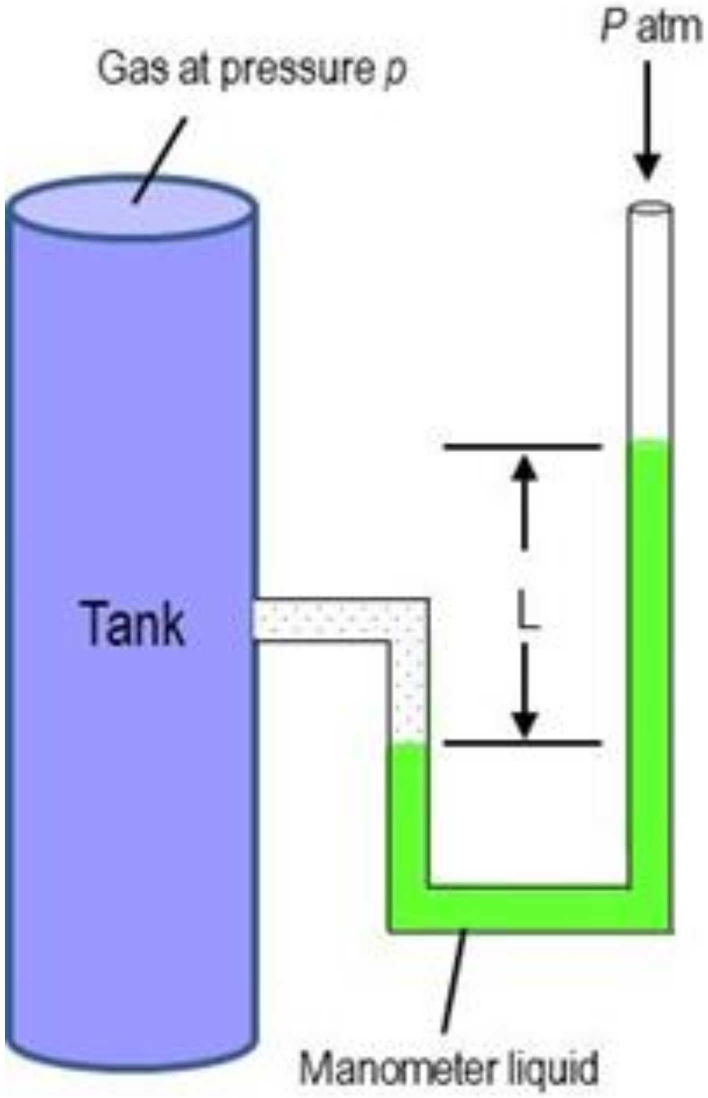
Pressure Measurement

- Two commonly used devices for measuring pressure are the **manometer and the Bourdon tube**.

- Manometers **measure pressure differences** in terms of the **length of a column of liquid** such as water, mercury, or oil.

Pressure Measurement

The manometer shown in Figure has one end open to the atmosphere and the other attached to a closed vessel containing a gas at uniform pressure.



Pressure Measurement

The difference between the gas pressure and that of the atmosphere is:

$$p = p_{atm} - \rho g L$$

where *ρ* is the density of the manometer liquid, *g* is the acceleration of gravity, and *L* is the difference in the liquid levels. For short columns of liquid, *ρ,* and *g* may be taken as constant.

Because of this proportionality between pressure difference and manometer fluid length, **pressures are often expressed in terms of millimeters of mercury**, inches of water, and so on.

Pressure Measurement - Example

The difference between the gas pressure and that of the atmosphere is:

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pressures are often expressed in terms of millimeters of mercury, inches of water, and so on.

Pressure Measurement

- The pressure of a sample of gas inside a container can be measured by using a pressure gauge, which is a device with electrical properties that depend on the pressure. For instance, a Bayard–Alpert pressure gauge is based on the **ionization of the molecules** present in the gas, and the resulting current of ions is interpreted in terms of the pressure.

- An important class of sensors utilizes the **piezoelectric effect**: A charge is generated within certain solid materials when they are deformed. This mechanical input /electrical output provides the basis for pressure measurement as well as displacement and force measurements.

- In a **capacitance manometer**, the deflection of a diaphragm relative to a fixed electrode is monitored through its effect on the capacitance of the arrangement. Certain semiconductors also respond to pressure and are used as transducers in solid-state pressure gauges.

Measuring Temperature

- The intensive property temperature is considered along with the means for measuring it. Like force, the concept of temperature originates with our sense perceptions. It is rooted in the notion of the “hotness” or “coldness” of a body.

- The concept of temperature springs from the observation that a change in physical state can occur when two objects are in contact with one another, as when a red-hot metal is plunged into water.

- We use our sense of touch to distinguish hot bodies from cold bodies and to arrange bodies in their order of “hotness,”. Accordingly, thermometers and temperature scales have been devised to measure it.

Measuring Temperature

- We shall see that the **state change** can be interpreted as arising from a **flow of energy** as heat from one object to another.

- The temperature, *T*, is the **property that indicates the direction of the flow of energy** through a thermally conducting, rigid wall.

- If energy flows from A to B when they are in contact, then we say that A has a higher temperature than B.

Thermal Equilibrium

- A definition of temperature in terms of concepts that are independently defined or accepted as primitive is difficult to give.

- It is possible to arrive at an objective understanding of equality of temperature by using the fact that when the temperature of a body changes, other properties also change.

Thermal Equilibrium - Example

- To illustrate this, consider two copper blocks, and suppose that our senses tell us that one is warmer than the other.

- If the blocks were brought into contact and isolated from their surroundings, they would interact in a way that can be described as a **thermal (heat) interaction**.

- During this interaction, it would be observed that the **volume** of the **warmer block decreases** somewhat with time, while the volume of the **colder block increases** with time. Eventually, **no further changes in volume would be observed, and the blocks would feel equally warm**.

Measuring Temperature - Example

- When all changes in such observable properties cease, the interaction is at an end.

- The two blocks are then in **thermal equilibrium**. Considerations such as these lead us to infer that the **blocks have a physical property** that determines whether they will be in thermal equilibrium.

- **This property is called temperature**, and we may postulate that when the **two blocks are in thermal equilibrium, their temperatures are equal**.

Thermal Equilibrium

- The rate at which the blocks approach thermal equilibrium with one another can be slowed by separating them with a thick layer. Although the rate at which equilibrium is approached can be reduced, **no actual material can prevent the blocks from interacting** until they attain the same temperature.

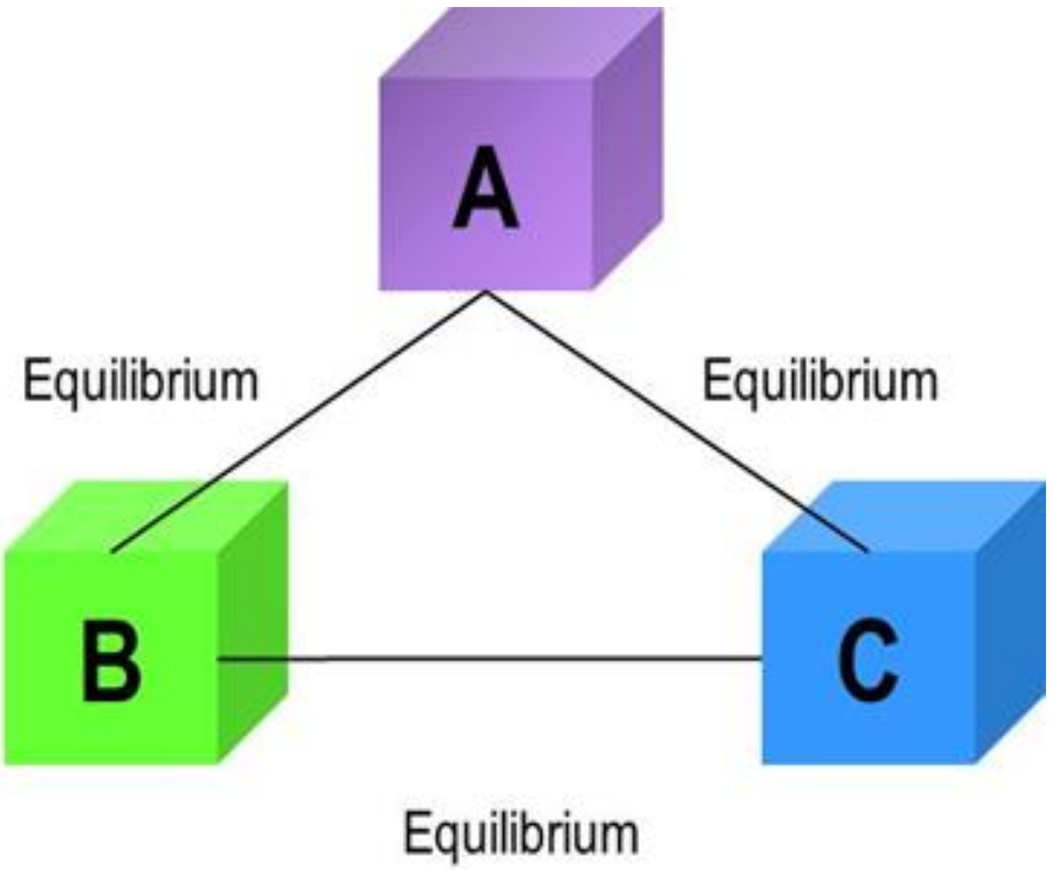
- **The temperature is a property that indicates whether two objects would be in 'thermal equilibrium'** if they were in contact through a diathermic boundary.

- **Thermal equilibrium** is established **if no change of state occurs** when two objects A to B are in contact through a diathermic boundary.

Thermal Equilibrium

Suppose object A is in thermal equilibrium with object B, and B is also in thermal equilibrium with another object C, then it has been found experimentally that A and C will also be in thermal equilibrium when they are put in contact.

This observation is summarized by **the Zeroth Law of thermodynamics**



Measuring Temperature

- Thus, if we want to know if two bodies are at the same temperature, it is not necessary to bring them into contact and see whether their observable properties change with time, as described previously.

- It is necessary only to see if they are individually in thermal equilibrium with a third body. **The third body is usually a thermometer.**

- **The Zeroth Law justifies the concept of temperature** and the use of a thermometer, a device for measuring the temperature. Thus, suppose that B is a glass capillary containing a liquid, such as mercury, that expands significantly as the temperature increases. Then, when A is in contact with B, the mercury column in the latter has a certain length.

Measuring Temperature

- According to the Zeroth Law, if the mercury column in B has the same length when it is placed in thermal contact with another object C, then we can predict that no change of state of A and C will occur when they are in thermal contact.

- We can use the length of the mercury column as a measure of the temperatures of A and C.

Remainder note

- An **ideal insulator** can be imagined that would preclude them from interacting thermally.

- An ideal insulator is called an adiabatic wall. When a system undergoes a process while enclosed by an **adiabatic wall**, it experiences no thermal interaction with its surroundings.

- Such a process is called an **adiabatic process**.

- A process that occurs at constant temperature is isothermal.

- An adiabatic process is not necessarily an **isothermal process**, nor is an isothermal process necessarily adiabatic.

Thermometers

- Any element with at least one measurable property that changes as its temperature changes can be used as a **thermometer**.
- Such a property is called a **thermometric property**.
- The substance that exhibits changes in the thermometric property is known as a **thermometric substance**.

Thermometers

- A familiar device for temperature measurement is the liquid-in-glass thermometer pictured in Figure, which consists of a glass capillary tube connected to a bulb filled with a liquid such as alcohol and sealed at the other end.

Thermometers

- The space above the liquid is occupied by the vapor of the liquid or an inert gas.
- As temperature increases, the liquid expands in volume and rises in the capillary. The length L of the liquid in the capillary depends on the temperature.
- Accordingly, the liquid is the thermometric substance and L is the thermometric property.

Thermometers

- Sensors known as **thermocouples** are based on the principle that when two dissimilar metals are joined, an electromotive force (emf) that is primarily a function of temperature will exist in a circuit.

- These sensors are since the electrical resistance of various materials changes in a predictable manner with temperature. The materials used for this purpose are normally conductors (such as platinum, nickel, or copper) or semiconductors. Devices using conductors are known as **resistance temperature detectors**.

- Semiconductor types are called **thermistors**. A variety of instruments measure temperature by sensing radiation, such as the ear thermometer. They are known by terms such as radiation thermometers and **optical pyrometers**.

Thermometric Scales

- Temperature scales are defined by the numerical value assigned to a standard fixed point.
-
- By international agreement the **standard fixed point is the easily reproducible triple point of water**: the state of equilibrium between steam, ice, and liquid water.
- As a matter of convenience, **the temperature at this standard fixed point is defined as 273.16 kelvin**, abbreviated as 273.16 K.

Thermometric Scales: Kelvin Scale, K

- The **Kelvin scale is an absolute thermodynamic temperature scale** that provides a continuous definition of temperature, valid over all ranges of temperature.
- Empirical measures of temperature, with different thermometers, can be related to the Kelvin scale.
- To develop the Kelvin scale, it is necessary to use the conservation of energy principle and the second law of thermodynamics.
- Kelvin scale has a **zero of 0 K**, and lower temperatures than this are not defined.

Thermometric Scales: Celsius Scale, ^{o}C

- The temperature interval from the ice point (273.15 K) to the steam point is equal to 100 K

- In agreement over the interval with the Celsius scale discussed next, which assigns 100 Celsius degrees to it. The kelvin is the SI base unit for temperature.

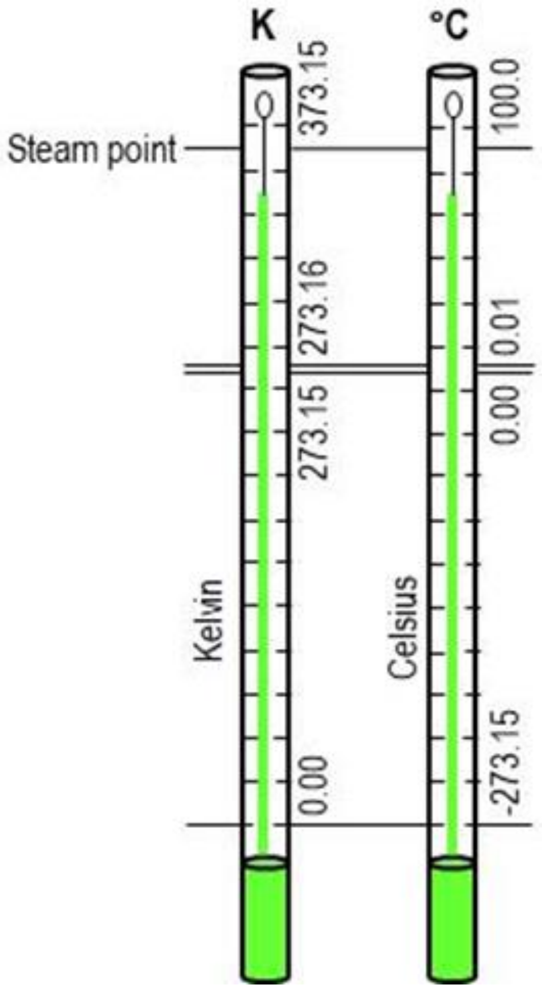
- The Celsius temperature scale (formerly called the centigrade scale) uses the unit degree Celsius (^{o}C), which has the same magnitude as the kelvin.

Thermometric Scales: Celsius Scale, ^{o}C

the zero point on the Celsius scale is shifted to 273.15 K, as shown by the following relationship between the Celsius temperature and the Kelvin temperature:

$$T(^{o}C) = T(K) - 273.15$$

From this on the Celsius scale, the triple point of water is 0.01 ^{o}C, and that 0 K corresponds to 273.15 ^{o}C.



The gas laws

The equation of state of gas at low pressure was established by combining a series of empirical laws. We assume that the following individual gas laws are familiar:

Boyle's law	pV = constant	constant n,T
Charles's law	V = (constant) T	constant n,p
	p = (constant) T	constant n,V
Avogadro's principle	V =(constant) n	constant p,T

The gas laws

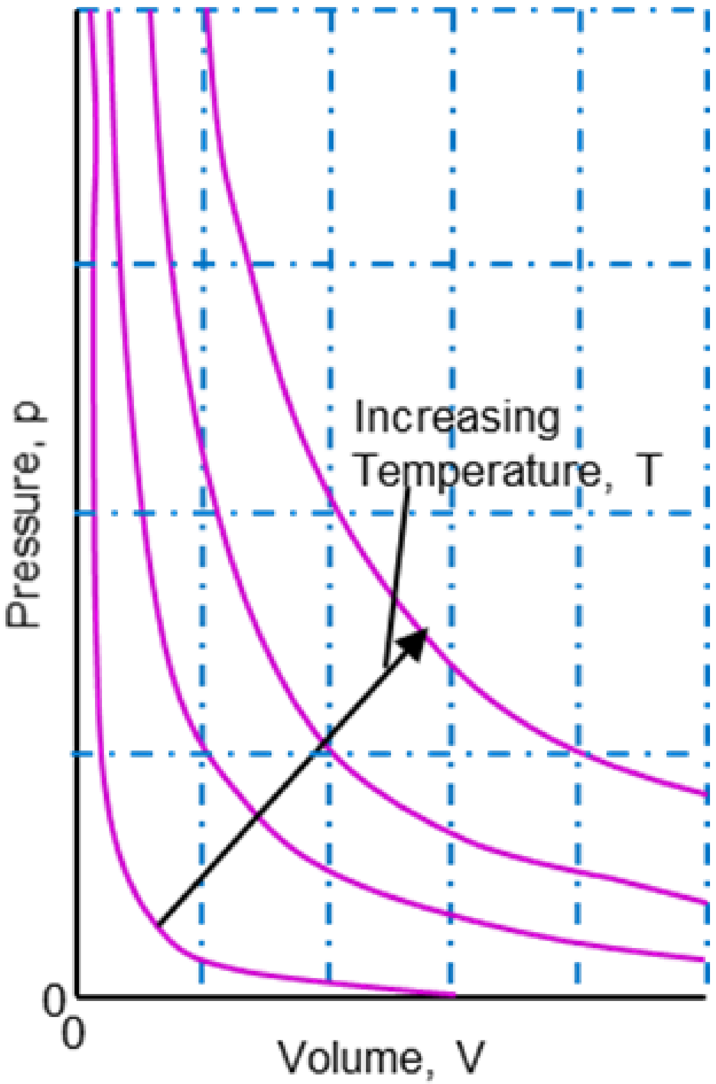
- Boyle's and Charles's laws are examples of a limiting law, a law that is strictly true only in a certain limit, in this case $p \rightarrow 0$.

- Avogadro's principle is commonly expressed in the form of "equal volumes of gases at the same temperature and pressure contain the same numbers of molecules".

- In this form, it is increasingly true as $p \rightarrow 0$. Although these relations are strictly true only at $p = 0$, they are reasonably reliable at normal pressures ($p \approx 1$ bar) and are used widely throughout chemistry.

The gas laws

The variation of the pressure of a sample of gas as the volume is changed. Each of the curves in the graph corresponds to a single temperature and hence is called an isotherm. According to Boyle's law, the isotherms of gases are hyperbolas.



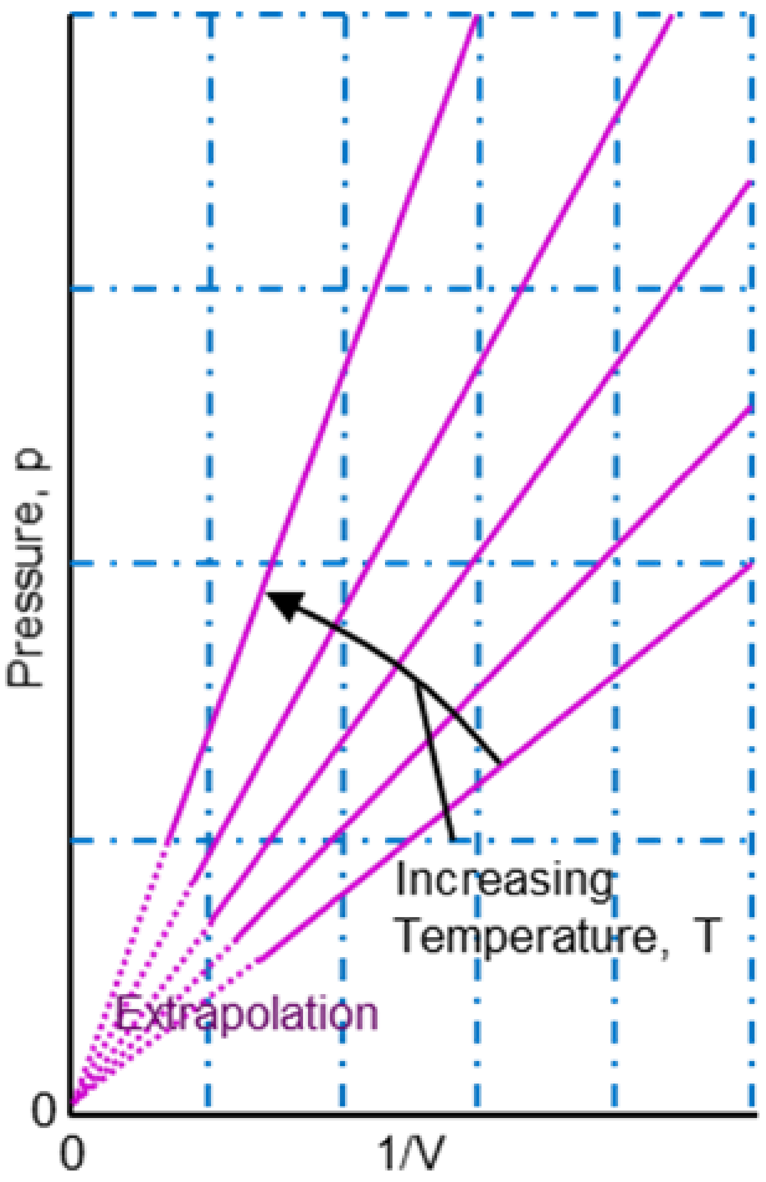
p = constant/V and constant n,T

The gas laws

An alternative depiction, a plot of pressure against 1/volume, is shown in Figure.

$$p = (1/V)\ \text{constant}$$

and constant n,T

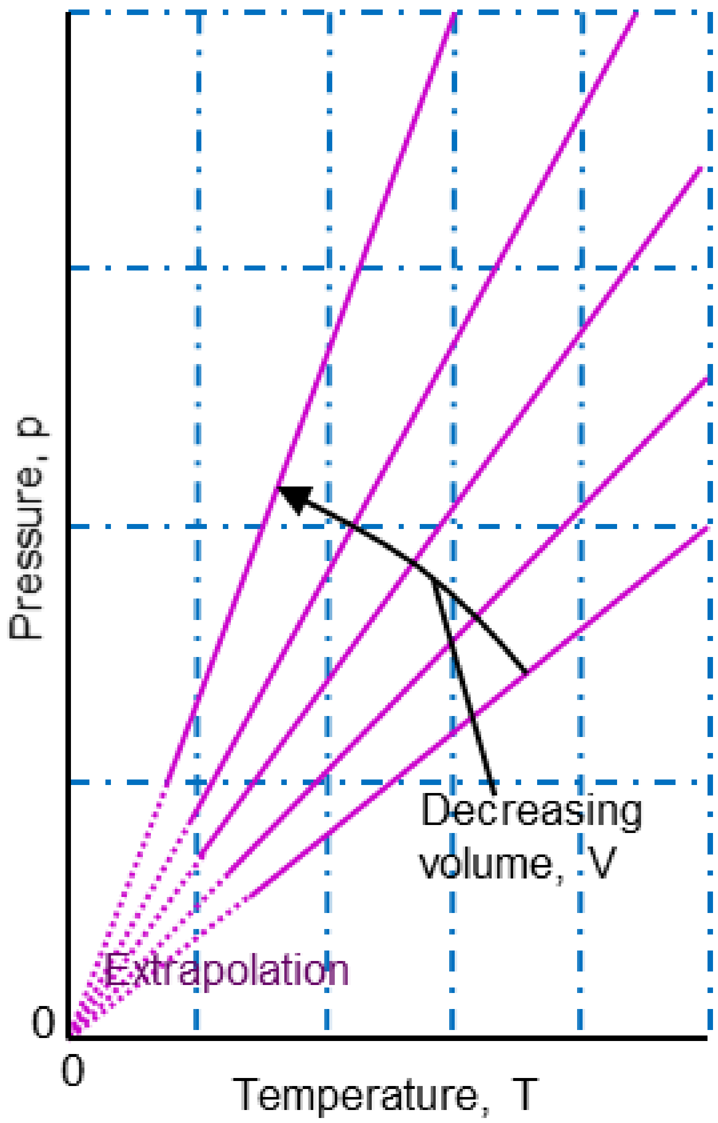


The gas laws

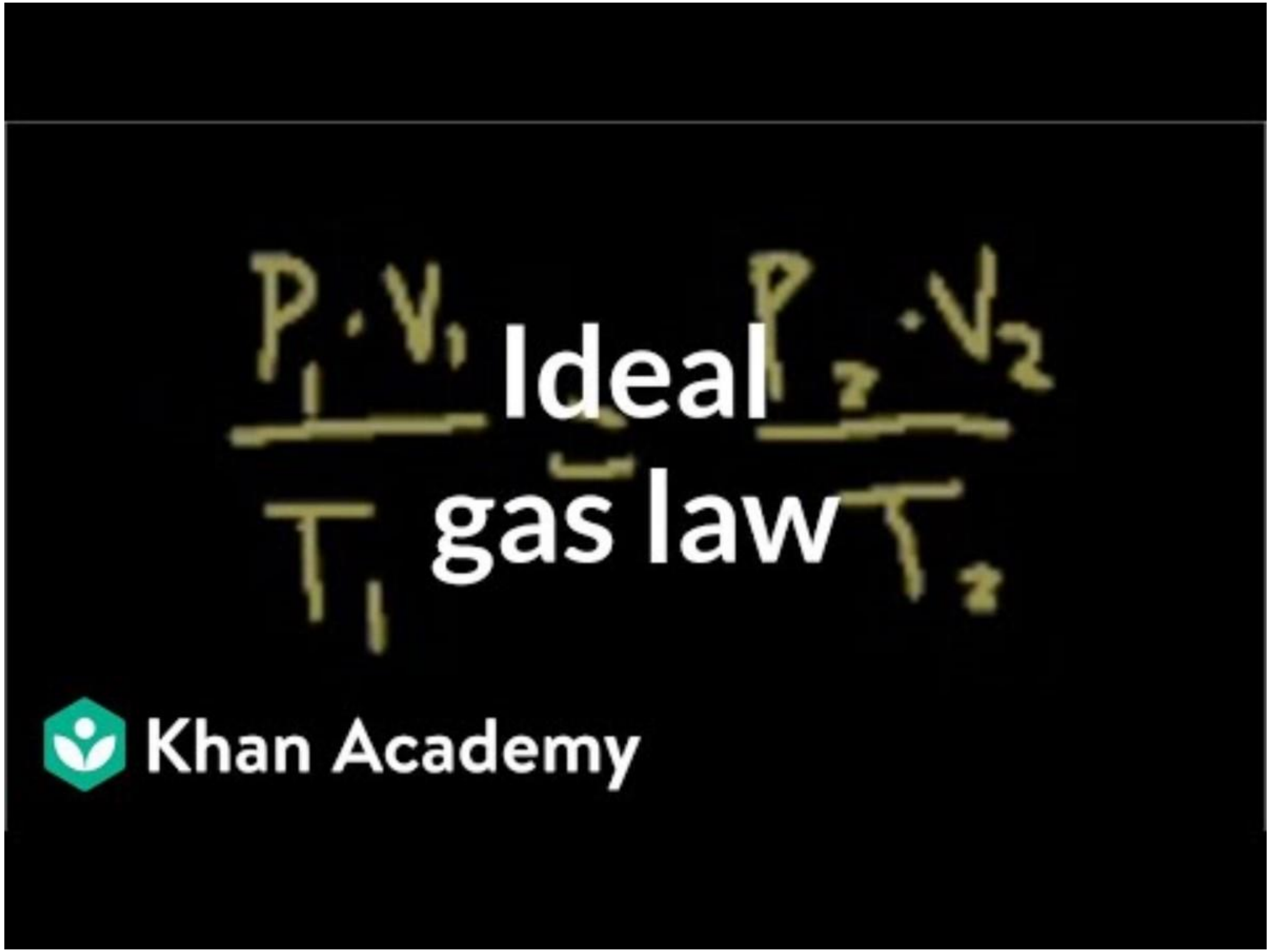
illustrates the linear variation of pressure with temperature. The lines in this diagram are isochores, or lines showing the variation of properties at constant volume.

$$p = (constant)\ T$$

And constant *n*,V



The gas laws



The gas laws

- The empirical observations summarized by all equations can be combined into a single expression:

$$pV = (\text{constant})nT$$

- This expression is consistent with Boyle's law (pV = constant) when n and T are constant, with both forms of Charles's law ($p \propto T$, $V \propto T$) when n and either V or p are held constant, and with Avogadro's principle ($V \propto n$) when p and T are constant.

The gas laws: ideal gas

The constant of proportionality, which is found experimentally to be the same for all gases, is denoted R and called the gas constant. The resulting expression:

$$pV = nRT$$

is **the perfect gas equation**. It is the approximate equation of the state of any gas and becomes increasingly exact as the pressure of the gas approaches zero. A gas that obeys this equation exactly under all conditions is called a perfect gas (or **ideal gas**).

The gas laws: ideal gas

- A real gas, behaves more like a perfect gas the **lower the pressure** and is described exactly by an ideal gas equation in the **limit of p → 0**.

- The **gas constant R** can be determined by evaluating R = pV/nT for a gas in the limit of zero pressure (to guarantee that it is behaving perfectly).

The gas laws: R value

The table lists the values of R in a variety of units.

R	Units
8.314 47	$J\ K^{-1} mol^{-1}$
$8.205\ 74\ \times\ 10^{-2}$	$dm^3\ atm\ K^{-1}\ mol^{-1}$
$8.314\ 47\ \times\ 10^{-2}$	$dm^3\ bar\ K^{-1}\ mol^{-1}$
8.314 47	$Pa\ m^3\ K^{-1}\ mol^{-1}$
1 62.364	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
1.987 21	$cal\ K^{-1}\ mol^{-1}$

Exercise: plot pressure versus specific volume for the isotherms

1000 kg of Argon (M_a = 39.95 g/mol) at 100 bar and 255 K is stored in a tank. If the pressure, *p*, V, and temperature, T, of the gas, are related by the ideal gas equation, T is in K, and *p* is in bar, determine the volume of the tank in m^3 and the specific volume, *v*, in m^3/kg. Also, plot pressure versus volume for the isotherm T = 255 K.

Exercise: plot pressure versus specific volume for the isotherms

Given Data:

Mass of Argon 1000 kg

Molar Mass of 39.95 g/mol = 0.03995 kg/mol

Pressure 100 bar = 100 x 10^5 Pa

Temperature 255 K

Exercise: plot pressure versus specific volume for the isotherms

Calculation of Moles of Argon:

$n = m/M_a$ = 1000 kg/0.03995 kg/mol = 25031.29 moles

Volume of the Argon Gas (Using Ideal Gas Law):

$V = n\mathrm{RT}/p$

Where R is the gas constant, 8.314 J/(mol·K)

Exercise: plot pressure versus specific volume for the isotherms

Volume of the Argon Gas (Using Ideal Gas Law):

$V = nRT/p$ where R is the gas constant, 8.314 J/(mol·K)

$V = (25031.29 \text{ moles}) (8.314 \text{ J/(mol·K)}) (255 \text{ K}) / (100 \times 10^5 \text{ Pa}) = 5.30 \text{ m}^3$

(1 J = 1 kg m^2/s^2 and 1 N = 1 kg m/s^2 and 1 J = 1 N m and 1 Pa = N/m^2)

Result:

The volume of the tank needed to store the argon is approximately 5.30 cubic meters.

Exercise: plot pressure versus specific volume for the isotherms

To generate the plots, one would calculate pressures for a range of volumes using the ideal gas law in Excel and plot them on a graph with pressure (P) on the y-axis and volume (V) on the x-axis.