

Engineering Chemistry
CHM 001
Spring 2020

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Credit

Level One : First Semester						
Code	Subject	Lecture (hr/wk)	Practical (hr/wk)	Tutorial (hr/wk)	Total cr	Contact hr
CHM 001	Engineering Chemistry	2	2	1	3	5

References

- 1- *Chemistry: The Central Science*, Theodore L. Brown et al., 2012, Pearson Prentice Hall, USA
- 2- *Inorganic Chemistry*, Shriver and Atkins, 2010, Oxford University Press.
- 3- *Chemical Process Industries*, Austin G. T., Shreve's, 1984, McGraw-Hill Book Co., 5th Ed.,

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Assessment

- **2h unseen written examination 40%**
- **Midterm Exam. 20%**
- **Quizzes, activity, attendance and performance 10%**
- **Lab work 30 %.**



Passing Criteria

- ✓ **60 % for the total course mark + 12/40 in Final exam**



Absence of 6 Lectures and/or lab dismiss the final unseen examination

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List of contents

- **Gases**
- **Solutions**
- **Chemical Equilibrium**
- **Mass and Energy Balance**
- **Electrochemistry**
- **Thermodynamics**
- **Chemical Industries**

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Revision

Basic Principles of Chemistry

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Matter and Chemistry

- **Matter** (the physical material of the universe) is anything that has a mass and occupies space.

Chemistry deals with **studying** ----- of matter:

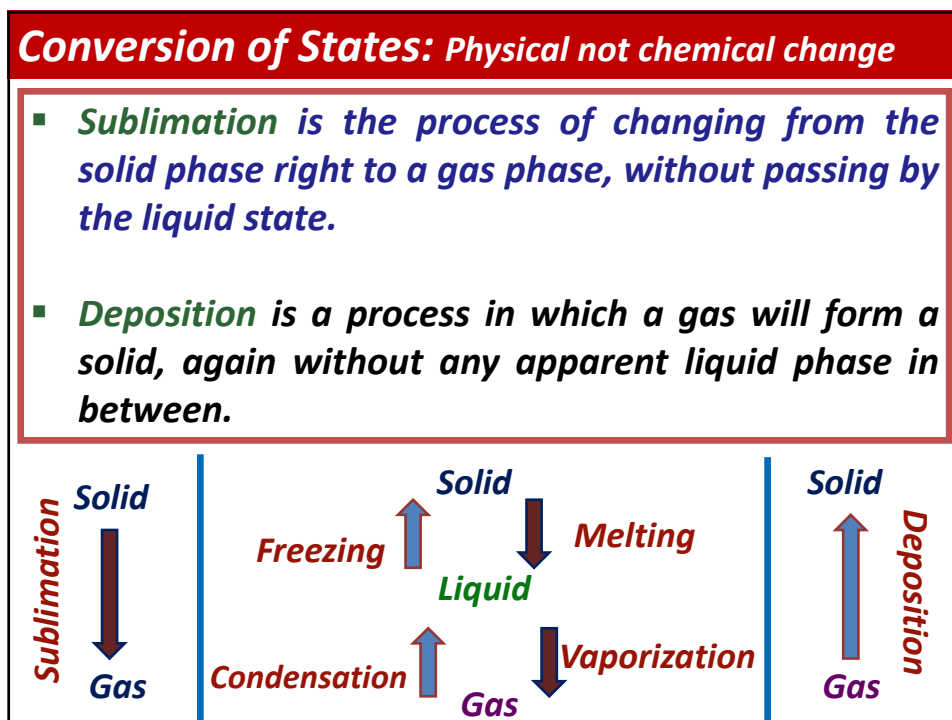
- Properties
- Composition, structure**
- Reactivity, behavior, changes

Tremendous variety of matter results from **118 elements**.

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Properties “Characteristics” of Matter			
Character	Solid	Liquid	Gas
Attraction	Strong	Intermediate	Very weak
Shape	Fixed	Not fixed	Not fixed
Volume	Fixed	Fixed	Not fixed, Highly dependent of P, T
Motion (Translation, Rotational, Vibrational)	V- Only vibrating	TR - Move around past each other	TRV Freely – randomly
Compressibility	No	little	high
KE	Lowest	Intermediate	Highest
Liquids and Solids: condensed phases			
Liquids and Gases: Fluids			

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Boiling Point

- The temperature at which a liquid boils and at which the vapor pressure of the liquid equal the **external** atmospheric pressure.

Normal Boiling Point

- The temperature at which a liquid boils and at which the vapor pressure of the liquid equal **1 atm**.

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Chemical Reactions/Balancing

- Reorganization of atoms in one or more substances.
- Mass is conserved in a chemical reaction.



Unbalanced

- Atoms are neither created nor destroyed



Balanced

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Reading Chemical Equations

	Reactants			Products			
	$\text{CH}_4(\text{g})$	+	$2\text{O}_2(\text{g})$	\rightarrow	$\text{CO}_2(\text{g})$	+	$2\text{H}_2\text{O}(\text{g})$
Molecules	1		2		1		2
Moles	1		2		1		2
Molecules /mole	6.022×10^{23}		$2 (6.022 \times 10^{23})$		6.022×10^{23}		$2 (6.022 \times 10^{23})$
g	16		2 (32)		44		2 (18)
Total mass	80				80		

Mass is conserved in a chemical reaction

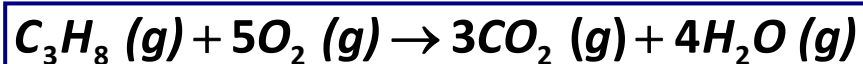
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Stoichiometric Calculations

Reaction of propane with oxygen: (Combustion)

“What mass of oxygen will react with 96.1 g of propane?”

Balance equation



Convert masses to moles:

$$96.1 \text{ g } \cancel{\text{C}_3\text{H}_8} \times \frac{1 \text{ mol } \text{C}_3\text{H}_8}{44.1 \text{ g } \cancel{\text{C}_3\text{H}_8}} = 2.18 \text{ mol } \text{C}_3\text{H}_8$$

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- ☐ Number of moles of O_2 necessary to react with 2.18 mole C_3H_8

$$2.18 \text{ mol } C_3H_8 \times \frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} = 10.9 \text{ mol } O_2$$

- ☐ Convert from moles to grams O_2

$$10.9 \text{ mol } O_2 \times \frac{32 \text{ g } O_2}{1 \text{ mol } O_2} = 349 \text{ g } O_2$$

- ☐ Therefore, 349 g O_2 is required to burn 96.1 g propane.

- What mass of carbon dioxide is produced when 96.1 grams of propane is combusted with oxygen?
(Homework)

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Units of measurements		<i>SI system</i> <small>French <i>Système International d'Unités.</i></small>	
7 SI Base UNITS	<i>from which all other units are derived</i>		
	Dimension	Unit	Unit Symbol
	Length	meter	<i>m</i>
	Mass	kilogram	<i>kg</i>
	Time	second	<i>s</i>
	Temperature	kelvin	<i>K</i>
	Electrical Current	ampere	<i>A</i>
	Amount of light	candela	<i>cd</i>
Amount of matter	mole	<i>mol</i>	
Recognize the capital and small letters			

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	Multiple	Prefix
Standard prefixes in SI Base units	10^{24}	yotta, Y
	10^{21}	zetta, Z
	10^{18}	exa, E
	10^{15}	peta, P
	10^{12}	tera, T
	10^9	giga, G
	10^6	mega, M
	10^3	kilo, k
	10^2	hecto, h
	10^1	deka, da
	10^{-1}	deci, d
	10^{-2}	centi, c
	10^{-3}	milli, m
	10^{-6}	micro, μ
	10^{-9}	nano, n
10^{-12}	pico, p	
10^{-15}	femto, f	
10^{-18}	atto, a	
10^{-21}	zepto, z	
10^{-24}	yocto, y	

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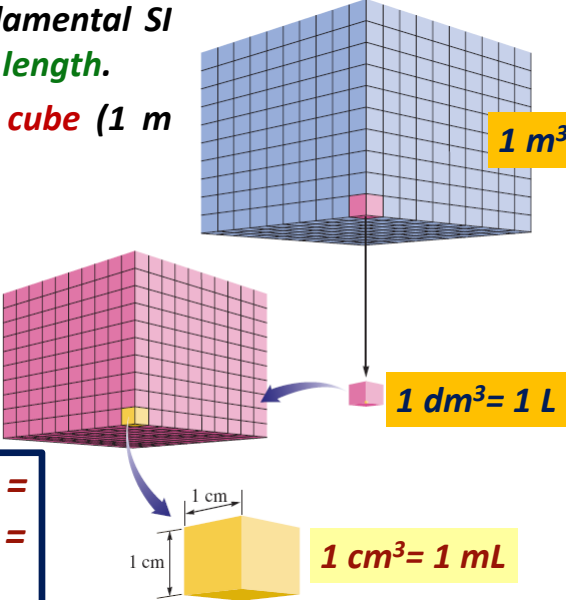
Exercises

- Which is the smallest: 1 mg, 1 μg , or 1 pg? **1 pg**
- What is the name of the unit that equals to (a) 10^{-9} g, (b) 10^{-6} s, (c) 10^{-3} m? **ng, μs , mm.**
- How many picometers are there in 1 m? **10^{12} pm**
- Express 6.0×10^3 m using a prefix to replace the power of ten? **6.0 km.**
- Use exponential notation to express 4.22 mg in grams? **4.22×10^{-3} g.**
- Use decimal notation to express 4.22 mg in grams? **0.00422 g**

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Derived SI Units (Volume)

- **Volume** is not a fundamental SI unit but derived from **length**.
- The **volume (V)** of a **cube** (1 m edge) = $(1\text{ m})^3 = 1\text{ m}^3$.
- As $1\text{ m} = 10\text{ dm}$,
 $V = (1\text{ m})^3 = (10\text{ dm})^3 = 1000\text{ dm}^3$.
- 1 dm^3 is commonly called a **liter (L)**



$1\text{ L} = (1\text{ dm})^3 = 1\text{ dm}^3 =$
 $(10\text{ cm})^3 = 1000\text{ cm}^3 =$
 $1000\text{ mL} = 1\text{ L}$

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Other Derived SI Units

Physical quantity	Symbol (s)	Name of SI unit	Derived Unit	Definition
Frequency	ν, f	Hertz	Hz	s^{-1}
Force	F	Newton	N	$\text{kg m s}^{-2} = \text{J m}^{-1}$
Energy	E, H, V, etc	Joule	J	$\text{N m} = \text{kg m}^2 \text{s}^{-2}$
Pressure	P	Pascal	Pa	$\text{N m}^{-2} = \text{kg m}^{-1} \text{s}^{-2}$
Power	p	Watt	W	$\text{J s}^{-1} = \text{kg m}^2 \text{s}^{-3}$
Charge	Q	Coulomb	C	A s
Potential	$E, \dots \text{etc}$	Volt	V	J A^{-1}
Resistance	R	Ohm	Ω	V A^{-1}
Conductance	G	Siemens	S	Ω^{-1}
Capacitance	C	Farad	F	C V^{-1}

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Other Units		
Physical quantity	Symbol	SI unit
Area	A	m ²
Volume	V	m ³
Velocity	U, V, c	m s ⁻¹
Acceleration	a, g	m s ⁻²
Weight	G, W	N
Density	ρ	kg m ⁻³
Volume	liter (l)	dm ³
Force	dyne (dyn)	10 ⁻⁵ N
Concentration	Molar (M)	mol dm ⁻³
Energy	Calorie (Cal)	4.18 J
Energy	Erg (erg)	10 ⁻⁷ J
Pressure	Atmosphere (atm)	1.013 x 10 ⁵ Pa
Pressure	(mm Hg)	133.322 Pa
Pressure	Torr (torr)	133.322 Pa
Pressure	Bar	10 ⁵ Pa
Pressure	Atmosphere	760 mm Hg = 76 cm Hg

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Temperature
<p><input type="checkbox"/> Temperature, is a physical property measuring the hotness or coldness of an object and determining the direction of heat flow.</p> <p><input type="checkbox"/> Heat always flows spontaneously from a substance of a higher temperature to another of a lower temperature. We feel the influx of heat when we touch a hot object.</p> <p><input type="checkbox"/> The temperature scales commonly employed in science are the Celsius and Kelvin scales.</p> <p><input type="checkbox"/> The Celsius scale was originally based on the assignment of 0 °C to the freezing point of water and 100 °C to its boiling point at sea level</p> <p><input type="checkbox"/> The SI unit of temperature is the Kelvin (K).</p>

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Absolute Temperature

Temperature at which the gas molecules stop to move

❑ Zero on the Kelvin scale is the lowest attainable temperature, $-273.15\text{ }^{\circ}\text{C}$, referred to as **absolute zero**.

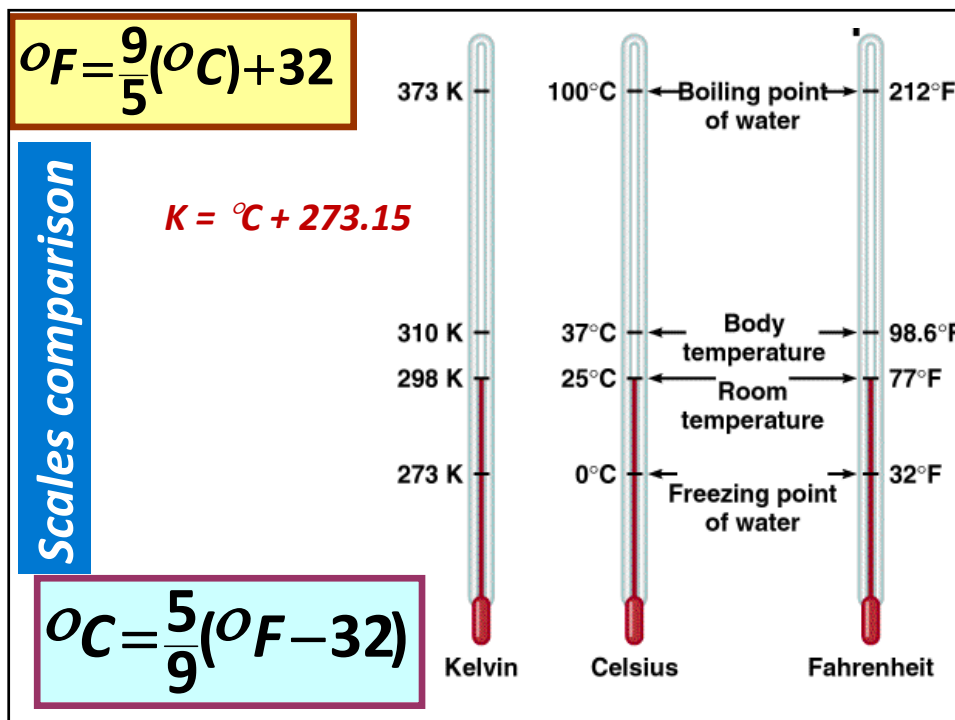
❑ The Celsius and Kelvin scales have equal-sized units.

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

❑ The common temperature scale in the United States is the **Fahrenheit** scale.

❑ Water freezes at **32** $^{\circ}\text{F}$ and boils at **212** $^{\circ}\text{F}$.

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Exercises

✚ How many mL are in 1.63 L?

$$1.63 \cancel{\text{L}} \times \frac{1000 \cancel{\text{mL}}}{1 \cancel{\text{L}}} = 1630 \text{ mL} = 1.63 \times 10^3 \text{ mL}$$

✚ The speed of sound in air is about 343 m/s. What is this speed in miles per hour?

$$343 \frac{\cancel{\text{m}}}{\cancel{\text{s}}} \times \frac{3600 \cancel{\text{s}}}{1 \text{ h}} \times \frac{1 \text{ mi}}{1609 \cancel{\text{m}}} = 767 \frac{\text{mi}}{\text{h}}$$

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Pressure

- ▶ is the normal **force** exerted by a **fluid** (gas or liquid) per unit **area**.
- ▶ It has the unit (N/m^2), which is called a **pascal** (**Pa**).
- ▶ **Pressure** is also used on solid surfaces as synonymous to **normal stress**.

- $1 \text{ bar} = 10^5 \text{ Pa} = 0.1 \text{ MPa} = 100 \text{ kPa}$

- $1 \text{ atm} = 101,325 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ bars} = 760 \text{ mm Hg} = 760 \text{ torr}$

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- In **CGS** system, P is measured in **dyne cm^{-2}**
- The **standard atmosphere** is the pressure exerted by a **76 cm** high column of mercury of **density $13.6 g cm^{-3}$** in a place where the acceleration due to gravity is **$980 cm s^{-2}$** .

$$\begin{aligned} \text{Pressure (1 atm)} &= \frac{\text{Force}}{\text{Area}} = \frac{\text{Mass} \times \text{Acceleration}}{\text{Area}} = \\ &= \frac{\text{Volume} \times \text{density} \times \text{Acceleration}}{\text{Area}} = \\ &= \text{Length} \times \text{density} \times \text{Acceleration} = \\ &= 76 \text{ cm} \times 13.6 \text{ g cm}^{-3} \times 980 \text{ cm s}^{-2} \\ &= 1.01325 \times 10^6 \text{ g cm}^{-1} \text{ s}^{-2} \text{ (dyne cm}^{-2}\text{)} \end{aligned}$$

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Pressure

- In **SI** system, P is measured in **$N m^{-2}$ (Pa: Pascal)**

$$\begin{aligned} \text{Pressure (1 atm)} &= \frac{\text{Force}}{\text{Area}} = \\ &= \text{Length} \times \text{density} \times \text{Acceleration} = \\ &= 0.76 \text{ m} \times 13.6 \times 10^4 \text{ kg m}^{-3} \times 9.8 \text{ m s}^{-2} \\ &= 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2} \text{ (N m}^{-2}\text{) (Pa)} \end{aligned}$$

$$\begin{aligned} 1 \text{ atm} &= 1.0325 \text{ bar} = 760 \text{ mmHg} = 760 \\ &= 760 \text{ torr} = 101,325 \text{ N/m}^2 = 101,325 \text{ Pa} \end{aligned}$$

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Exercise (Pressure conversion)

✚ The pressure of a gas is measured as 49 torr. Represent this pressure in both atmospheres and pascals?

$$49 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 6.4 \times 10^{-2} \text{ atm}$$

$$6.4 \times 10^{-2} \text{ atm} \times \frac{101,325 \text{ Pa}}{1 \text{ atm}} = 6.5 \times 10^3 \text{ Pa}$$

The state of a gas can be fully described in terms of **4 variables** (Mass, Volume, Pressure, Temperature). By knowing 3 of them, the fourth can be calculated

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Chapter 1

Gaseous State

Kinetic theory of gases

Gases' laws

ideal and real gases

Compressibility factor

Gases' mixtures

Clapeyron equation

Gases' Liquefaction

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Chapter 1: Gaseous State

1.1 The Kinetic theory of gases

1.2 Gases' laws

1.3 General law for ideal gases

1.4 Real Gases

1.5 Gas mixture

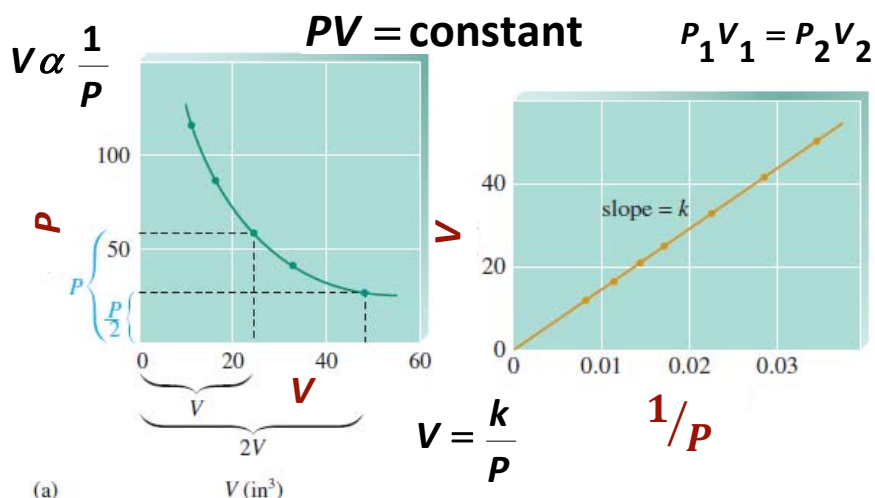
1.6 Clapeyron equation

1.7 Liquefaction of gases

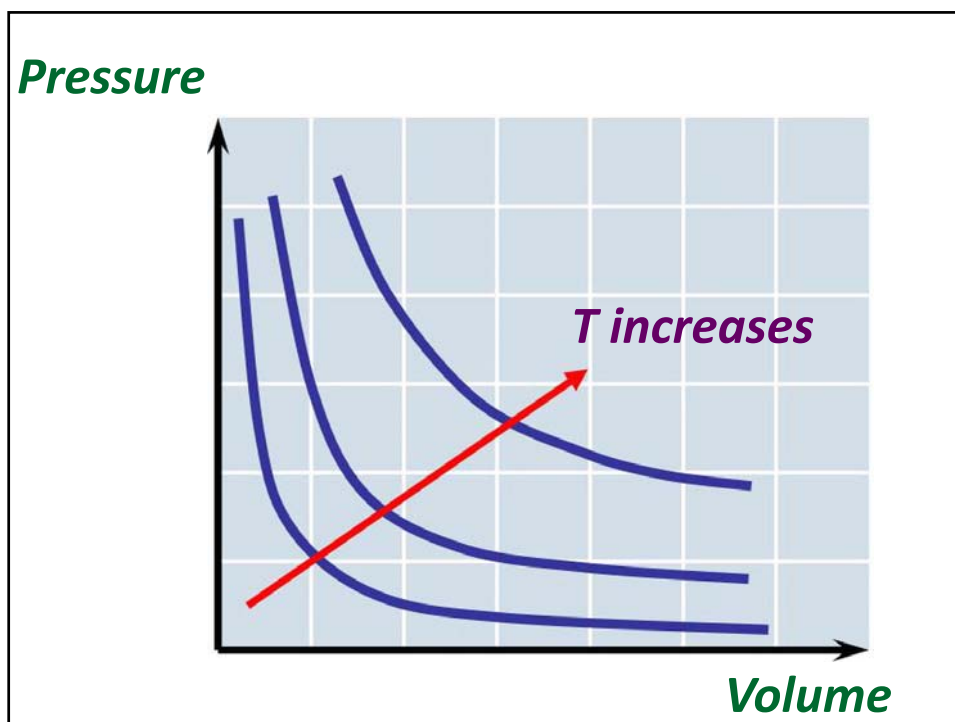
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Boyle's Law

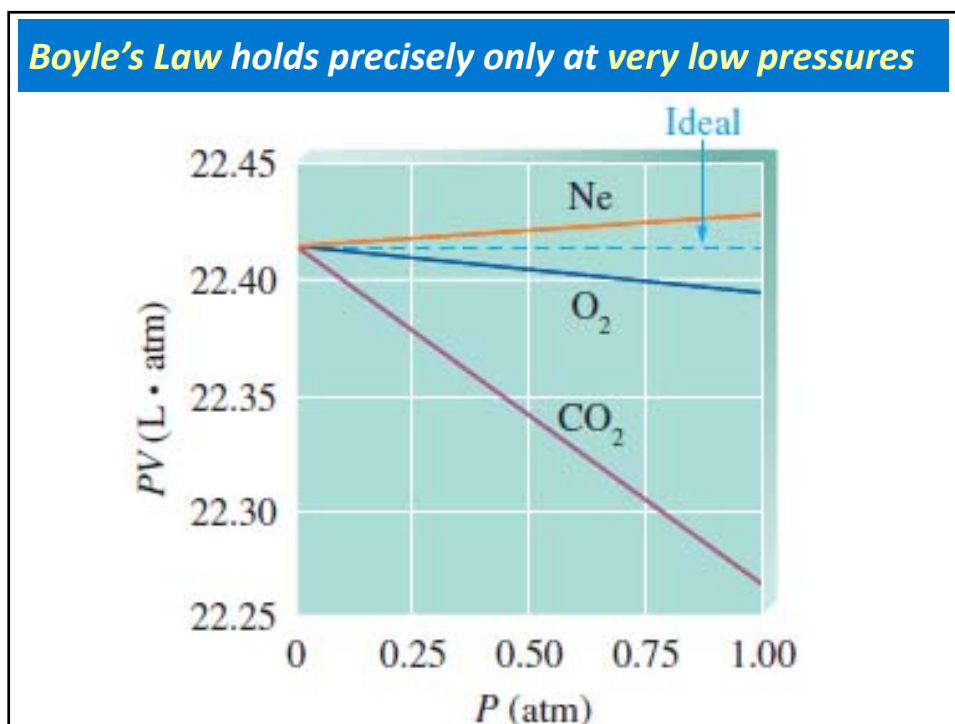
At a **constant temperature**, the volume of a **fixed amount** of gas is **inversely** proportional to its pressure.



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Exercise: Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.53 L sample of gaseous SO_2 at a pressure of $5.6 \times 10^3 \text{ Pa}$. If the pressure is changed to $1.5 \times 10^4 \text{ Pa}$ at a constant temperature, what will be the new volume of the gas?

Solution

$$P_1 = 5.6 \times 10^3 \text{ Pa} \quad \longrightarrow \quad V_1 = 1.53 \text{ L}$$

$$P_2 = 1.5 \times 10^4 \text{ Pa} \quad \longrightarrow \quad V_2 = ? \text{ L}$$

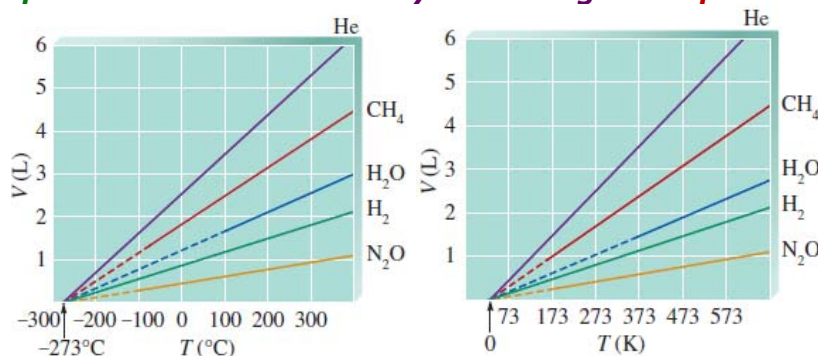
$$P_1 V_1 = P_2 V_2 \quad V_2 = \frac{P_1 V_1}{P_2} = \frac{5.6 \times 10^3 \cancel{\text{Pa}} \times 1.53 \text{ L}}{1.5 \times 10^4 \cancel{\text{Pa}}} = 0.57 \text{ L}$$

V decreases ✓

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Charles's Law

The **volume** of a **fixed** amount of a gas at a constant **pressure** increases linearly with the gas **temperature**



✓ **Different Slopes:** because of different numbers of moles of gas.

✓ **Volumes** of gases extrapolate to zero at the same temperature, $-273^\circ\text{C} = 0 \text{ K}$ (**absolute Zero**), $\text{K} = ^\circ\text{C} + 273$

$$V \propto T$$

$$\frac{V}{T} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

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Exercise

A sample of gas at 15°C and 1 atm has a volume of 2.58 L. What volume will this gas occupy at 38°C and 1 atm?

Solution

P and $n = \text{constant}$

$$V_1 = 2.58\text{L} \longrightarrow T_1 = 15^\circ\text{C} + 273 = 288\text{K}$$

$$V_2 = ?\text{L} \longrightarrow T_2 = 38^\circ\text{C} + 273 = 311\text{K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

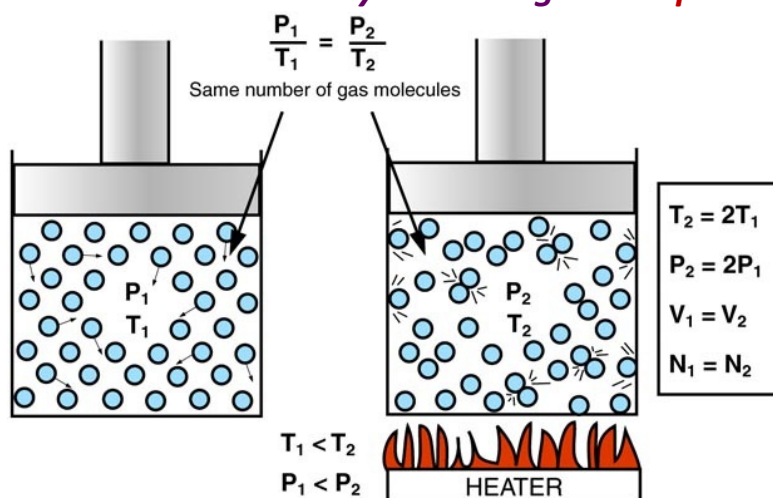
$$V_2 = \frac{V_1 T_2}{T_1} = \frac{2.58\text{L} \times 311\text{K}}{288\text{K}} = 2.79\text{L}$$

V increases ✓

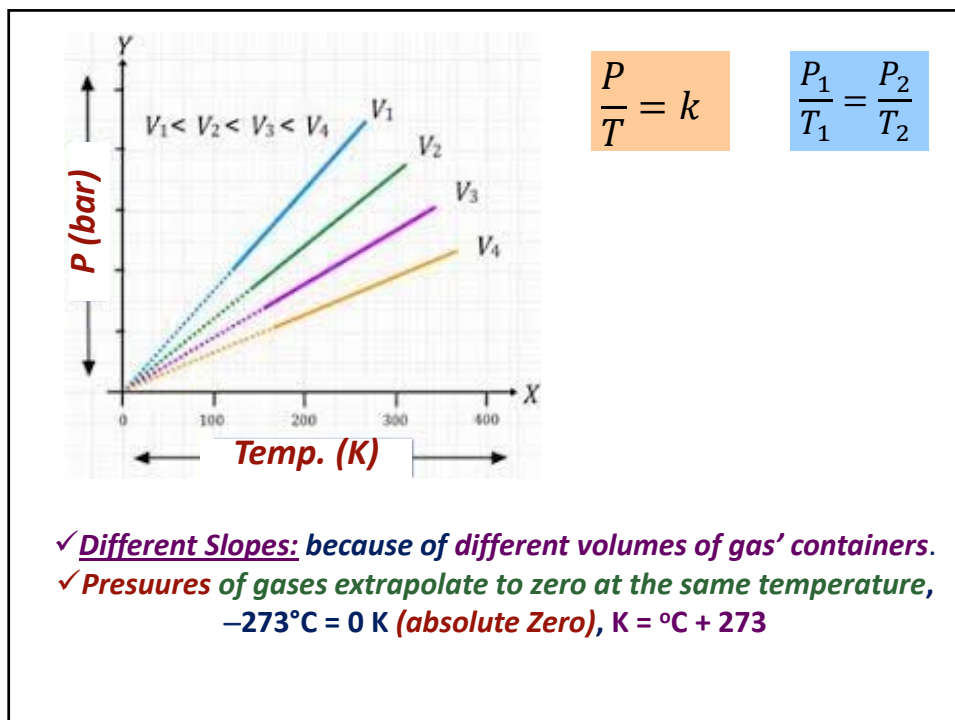
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Gay-Lussac's Law (constant n, V)

The pressure of a fixed amount of a gas at a constant volume increases linearly with the gas' temperature



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Avogadro's Law


Equal volumes of gases at the same temperature and pressure contain the same number of "particles".

OR


$V \propto n$ $\frac{V}{n} = k$ $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

For a gas at constant T and P , the volume is directly proportional to its number of moles.


N_2




H_2



Ar



CH_4



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Exercise: Suppose we have a **12.2 L** sample containing **0.50 mole** of oxygen gas (O_2) at a pressure of **1 atm** and a temperature of **25°C**. If all this O_2 were converted to **0.33 mole** of ozone (O_3) at the same temperature and pressure, what would be the volume of the ozone?

P and T = constant

Solution

$$V_1 = 12.2L \quad \longrightarrow \quad n_1 = 0.5 \text{ mol } O_2$$

$$V_2 = ?L \quad \longrightarrow \quad n_2 = 0.33 \text{ mol } O_3$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad V_2 = \frac{V_1 n_2}{n_1} = \frac{12.2L \times 0.33 \text{ mol}}{0.5 \text{ mol}} = 8.1L$$

V decreases ✓

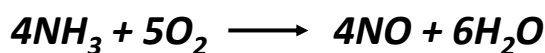
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Exercise

Exercise: Ammonia burns in oxygen to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?

P and T = constant

Solution



At constant T and P



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The Ideal Gas Law

Boyle's law: $V = \frac{k}{P}$ (constant T, n)

Charles's law: $V = bT$ (constant P, n)

Avogadro's law: $V = an$ (constant T, P)

$$V = R \left(\frac{Tn}{P} \right)$$

$$PV = nRT$$

Equation of
state for gases

R : Universal
gas constant

$$R = \frac{0.08206 \text{ L atm}}{\text{K mol}}$$

This equation is mostly obeyed at **low pressures and high temperatures**

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Universal Gas Constant / R

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.414 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} =$$

$$0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$= 82 \text{ mL atm K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$$

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Dalton's Law of Partial Pressures


"For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone"

Assuming ideal behavior

$$\begin{aligned}
 P_{\text{Total}} &= P_1 + P_2 + P_3 + \dots \\
 &= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \dots \\
 &= \left(n_1 + n_2 + n_3 + \dots \right) \frac{RT}{V} = \frac{n_{\text{Total}} RT}{V}
 \end{aligned}$$

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Dalton's Law

 The **pressure** exerted by an ideal gas is **not affected** by the **identity (composition)** of the gas particles. **This reveals:**

- ▶ **The volume of the individual gas particle is not important**
- ▶ **The forces among the particles must not be important.**

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Exercise: Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent “the bends.” For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O₂ at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Solution

$$n_{\text{He}} = \frac{(1.0 \text{ atm})(46 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 1.9 \text{ mol}$$

$$n_{\text{O}_2} = \frac{(1.0 \text{ atm})(12 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 0.49 \text{ mol}$$

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Calculate the partial pressure for each gas in the tank

$$P_{\text{He}} = \frac{(1.9 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})}{(5 \text{ L})} = 9.3 \text{ atm}$$

$$P_{\text{O}_2} = \frac{(0.49 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})}{(5 \text{ L})} = 2.4 \text{ atm}$$

$$P_T = P_{\text{He}} + P_{\text{O}_2} = 9.3 + 2.4 = 11.7 \text{ atm}$$

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Mole fraction, χ

The **ratio** of the number of moles of a given component in a mixture to the total number of moles in the mixture.

$$\chi_1 = \frac{n_1}{n_T} = \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$

$$= \frac{(V/RT)P_1}{(V/RT)(P_1 + P_2 + P_3 + \dots)}$$

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Mole fraction, χ

$$\chi_1 = \frac{P_1}{(P_1 + P_2 + P_3 + \dots)} = \frac{P_1}{P_T}$$

► **The mole fraction** of each component in a mixture of ideal gases is directly related to its partial pressure

$$\chi_2 = \frac{n_2}{n_T} = \frac{P_2}{P_T}$$

$$\sum_i \chi_i = 1$$

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Example

- The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present at 25°C ?

Answer

$$\chi_{O_2} = \frac{P_{O_2}}{P_T} = \frac{156 \text{ torr}}{743 \text{ torr}} = 0.210$$

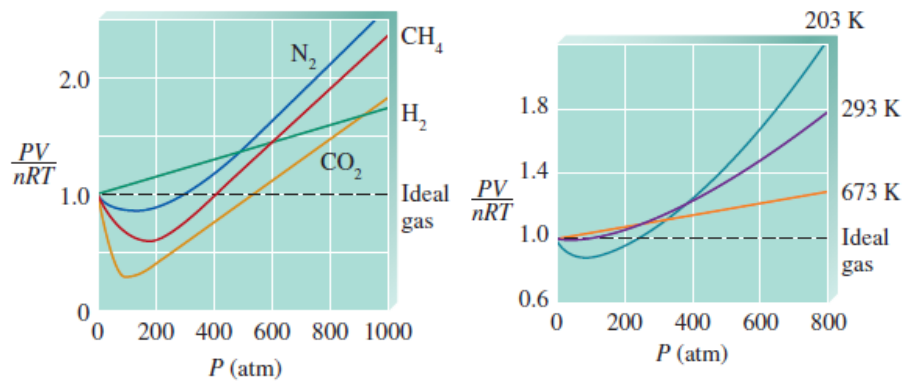
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Kinetic Molecular Theory (KMT) of Gases Postulates

- 1) A gas is composed of a **large** number of **small** (relative to distance between them) **particles** that behave like **hard** (point masses: no structure, no volume and no size), **spherical** objects—have **negligible volume**
- 2) The particles are in **constant random** (straight-line) free motion involving **frequent elastic** “particle’s kinetic energy is not lost” **collisions** with each other and with the **walls** of the container (origin of **pressure**)
- 3) **Attractive and repulsive forces** between molecules are negligible. (Particles have a great freedom to move)
- 4) The average **kinetic energy** of gas particles is **directly proportional only** to the **absolute** “Kelvin” **temperature** of the gas.

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Real Gases



- ✦ Almost all gases deviate from the ideal behavior, particularly at high pressure and low temperature.
- ✦ A real gas typically exhibits behavior that is closest to ideal behavior at low pressures and high temperatures.

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Volume Correction

- ◆ The **KMT** assumed a **zero volume** for the gas molecules under any condition !!!!!!! **Wrong?**
- ◆ The **non-zero volume** of molecules implies that **instead of moving in volume V** they are restricted to a smaller volume $V - nb$, where nb is approximately the total volume taken up by the molecules themselves.
- ◆ This replaces
$$p = \frac{nRT}{V} \rightarrow p' = \frac{nRT}{V - nb}$$
- b (molar volume) is a constant characteristic of each gas.
- ◆ **HCl** would have a slightly larger "**b**" correctional factor than **H₂**

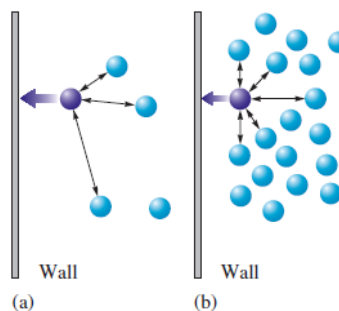
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Pressure Correction

❑ The KMT assumed neither attraction nor repulsive forces (zero potential energy) between gas molecules under any condition !!!!!!! **Wrong?**

✓ The effect of these attractions is to make the observed pressure P_{obs} smaller than it would be if the gas particles did not interact.

Low concentration
Low pressure
Ideal behavior



High concentration
High pressure
Real behavior

$$p_{obs} = p' - \text{correction factor} = \frac{nRT}{V - nb} - \text{correction factor}$$

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Correction factor of pressure

frequency of collisions with the walls $\propto \frac{n}{V}$

molarity $\propto \frac{n}{V}$

force of each collision $\propto \frac{n}{V}$

$$\text{Correction factor} \propto \left(\frac{n}{V}\right)^2 = a \left(\frac{n}{V}\right)^2$$

$a \left(\frac{n}{V}\right)^2$ is the internal pressure of the gas

$\left(\frac{V}{n}\right)$ molar volume of the gas

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The Van der Waals equation/Real gas eqn.

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a \left[\frac{n}{V} \right]^2$$

$$\left[P_{\text{obs}} + \frac{an^2}{V^2} \right] (V - nb) = nRT$$

$a_{(\text{HCl})} > a_{(\text{H}_2)}$ because HCl is a polar molecule and therefore has stronger intermolecular forces than H_2 .

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Gases behave ideally at low P and high T

At low P (large V), $V \gg nb$, $\longrightarrow V - nb \approx V$
Gas behaves ideally

At high P (small V) $\left\{ \begin{array}{l} \text{Significant particles' volume} \\ \text{Gas moves in a volume } \ll V \end{array} \right.$

At high T $\left\{ \begin{array}{l} \text{Particles are moving so rapidly} \\ \text{Effects of interparticle interactions are not very important (ideal)} \end{array} \right.$

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Molar Volume at STP

□ At standard temperature and pressure, **STP** (1 atm and 0°C), the molar volume of ideal gases is given by

$$V = \frac{nRT}{P} = \frac{(1.0 \text{ mol}) \left(\frac{0.08206 \text{ L atm}}{\text{K mol}} \right) (273 \text{ K})}{1.0 \text{ atm}} = 22.4 \text{ L}$$

Standard ambient temperature and pressure, SATP

SATP (1 bar and 25°C)

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Molar Mass of a Gas/Gas density

$$n = \frac{\text{mass (g)}}{\text{molar mass (g/mol)}} = \frac{m}{M}$$

$$P = \frac{nRT}{V} = \frac{\left(\frac{m}{M} \right) RT}{V} = \left(\frac{m}{V} \right) \left(\frac{RT}{M} \right) = \frac{dRT}{M}$$

$$M = \frac{dRT}{P}$$

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Exercise

The density of a gas was measured at 1.50 atm and 27 °C and found to be 1.95 g/L. Calculate the molar mass of the gas

Solution

$$M = \frac{dRT}{P}$$

$$= \frac{\left(1.95 \frac{\text{g}}{\text{L}}\right) \left(\frac{0.08206 \text{ L atm}}{\text{K mol}}\right) (300 \text{ K})}{1.0 \text{ atm}}$$

$$= 32.0 \frac{\text{g}}{\text{mol}}$$

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Exercises: The Van der Waals constants for Ar are listed below:

Substance	a ($\text{L}^2 \cdot \text{atm mol}^{-2}$)	b (L mol^{-1})
Ar	1.337	3.2

Using the Van der Waals equation, calculate the pressures exerted by 1.00 mole of Ar gas in a 22.4 L container at 273 K. How much is the pressure deviation from ideal behavior? Which is most likely behind the deviation from ideal behavior: the volumes of the molecules or intermolecular attractions?

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$$p = \frac{nRT}{V - nb} - a \left[\frac{n}{V} \right]^2$$

$$p = \frac{(1 \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{22.4 \text{ L} - [(1 \text{ mol}) \cdot (3.2 \text{ L mol}^{-1})]} - 1.337 \left[\frac{1 \text{ mol}}{22.4} \right]^2$$

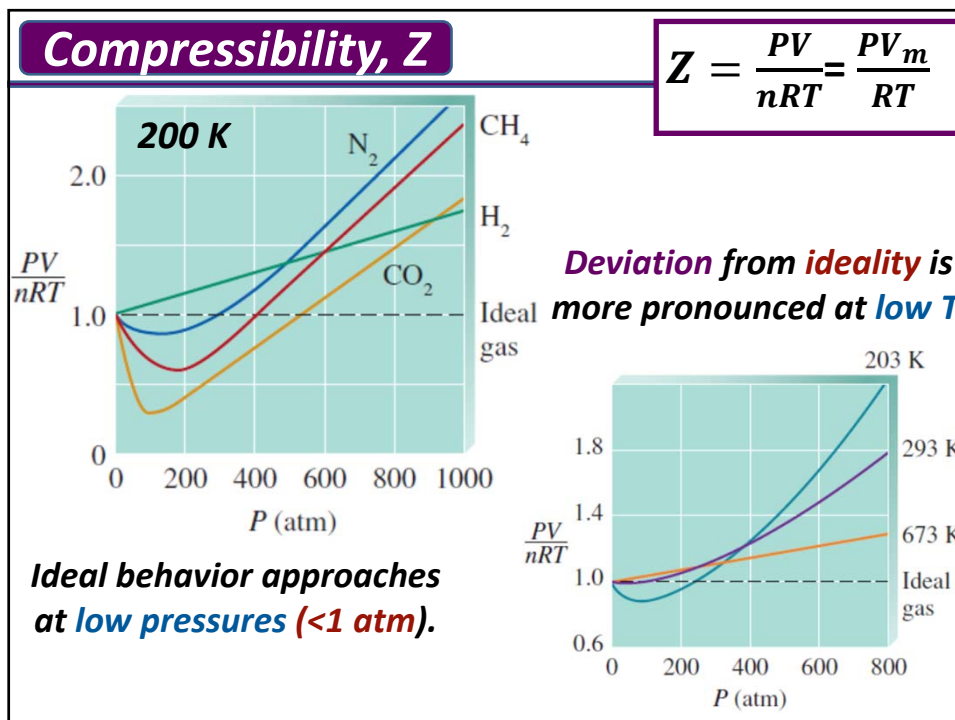
$P = 1.1674 - 0.00266 = 1.1648 \text{ atm}$

Under ideal behavior ($PV = nRT$) \longrightarrow $P = 1 \text{ atm}$

In the real case, the pressure correction (0.00266 atm) is very small; indicating that the main cause for deviation from ideal behavior is due to the **volumes** of the molecules rather than **intermolecular attractions**.

Ar (noble gas) has only the very weak **London dispersion forces**

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Critical temperature, T_c

Temperature **above** which vapors of a substance can not be liquified, no matter how **much pressure** is applied

Critical pressure, P_c

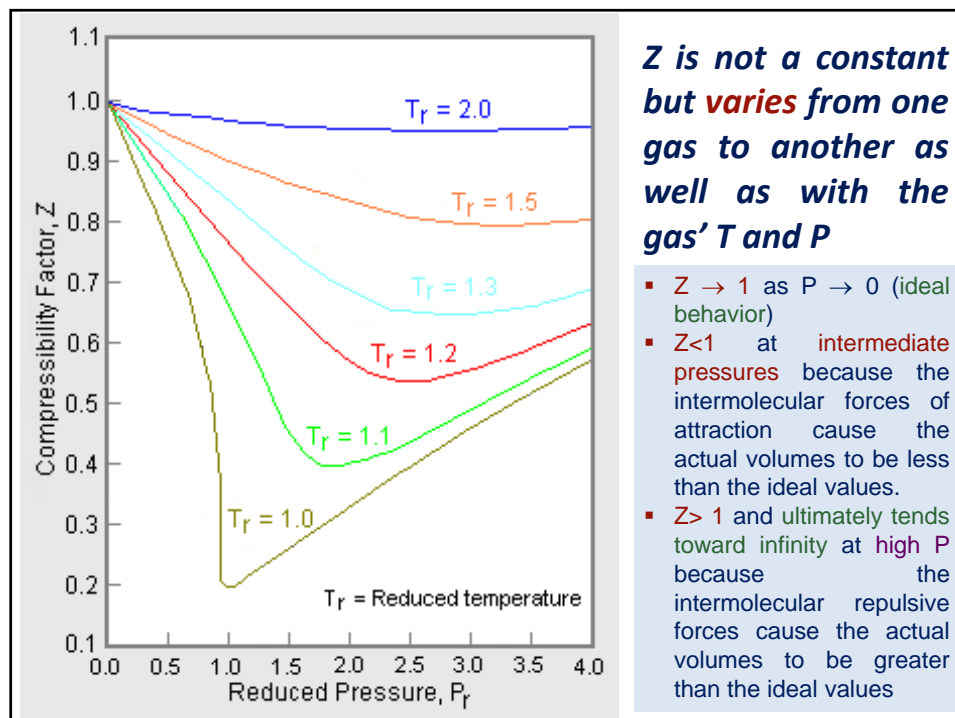
Pressure required to liquify a gas of a given substance **at its critical temperature**

$$\text{Reduced Pressure } (P_r) = \frac{P}{P_c}$$

$$\text{Reduced Volume } (V_r) = \frac{V_m}{V_c}$$

$$\text{Reduced Temp. } (T_r) = \frac{T}{T_c}$$

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Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

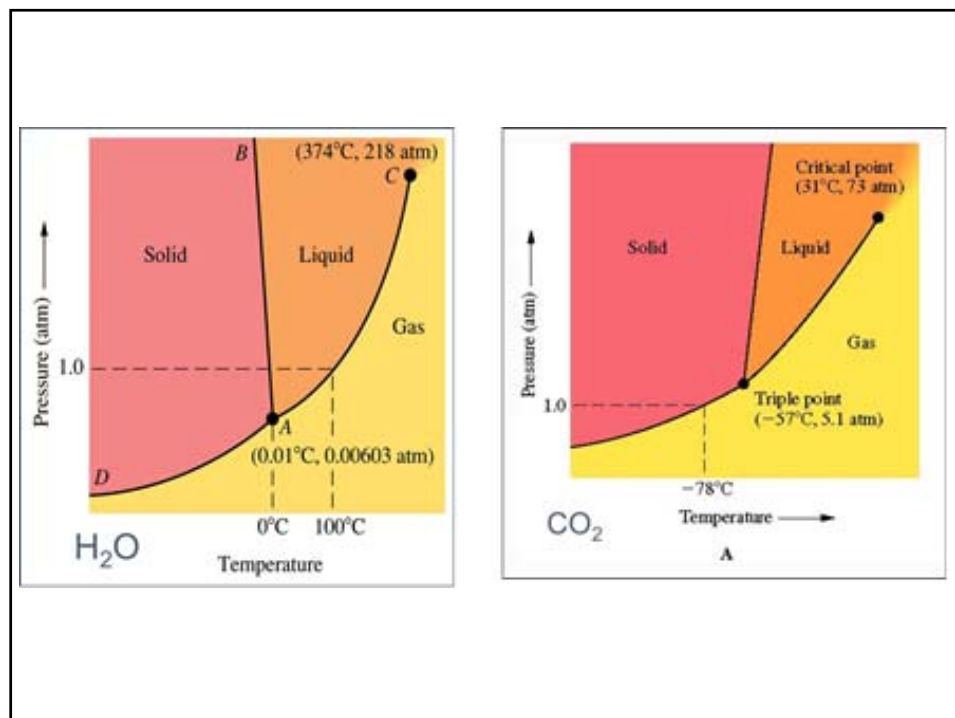
- It estimates the rate at which the vapor pressure changes with T .
- L : Latent heat of vaporization per mol.
- ΔV : molar volume change ($\Delta V = V_{\text{vapor}} - V_{\text{liquid}}$ when a liquid evaporates).

When a liquid evaporates At $T < T_c$ \rightarrow

$$V_{\text{vapor}} > V_{\text{liquid}} \quad \Delta V = +ve \quad L = +ve$$

Then $\frac{dP}{dT}$ should be $+ve$

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If T is far from T_c and assuming ideal behavior

$$V_{\text{vapor}} \gg V_{\text{liquid}}$$

$$\Delta V = V_{\text{vapor}} - V_{\text{liquid}} \approx V_{\text{vapor}} = \frac{RT}{P} \quad n = 1$$

$$\frac{dP}{dT} = \frac{L}{T \Delta V} = \frac{LP}{RT^2}$$



$$\frac{dP}{P} = \frac{L}{R} \frac{dT}{T^2}$$

$$d \ln P = \frac{L}{R} \frac{dT}{T^2}$$



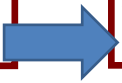
$$\frac{d \ln P}{dT} = \frac{L}{RT^2}$$

$$\int d \ln P = \int \frac{L}{R} \frac{dT}{T^2}$$

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► If L is known as a function of T , we can substitute easily. Otherwise, assume it **independent of T** over a limited small range of T

$$\ln p = \frac{-L}{R} \frac{1}{T} + \text{const}$$



$$\ln \frac{P_2}{P_1} = \frac{L}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

✚ As $T \uparrow$, $(1/T) \downarrow$, $P \uparrow$ exponentially.

✚ It corresponds to variation of vapor pressure of liquids with T

$$\ln \frac{P_2}{P_1} = \frac{L}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{P_2}{P_1} = \frac{L}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

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Exercise

✚ It is desired to produce superheated steam at 120 °C. Under what pressure water must be boiled to achieve this? Normal boiling point of water = 100 °C. The latent heat of vaporization of water = 39.70 kJmol⁻¹.

Answer

Normal boiling point of water (100 °C) corresponds to a pressure of 1 atm

$$\ln \frac{P_2}{P_1} = \frac{L}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log \frac{P_2}{1} = \frac{39700 \text{ Jmol}^{-1}}{2.303(8.314 \text{ JK}^{-1}\text{mol}^{-1})} \left(\frac{393 - 373}{393 \times 373} \right)$$

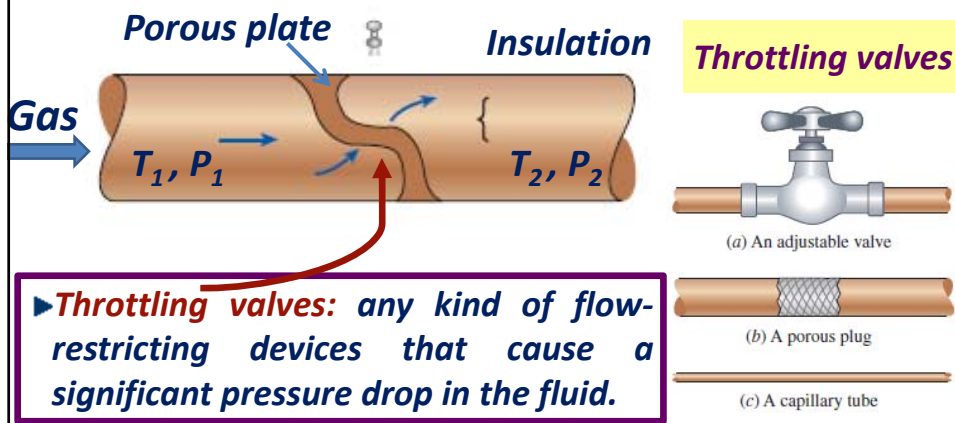
$$P_2 = 1.92 \text{ atm}$$

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Liquefaction of gases

1 - Joule-Thomson effect

✚ When a fluid passes through a **restriction** such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases.



► **Throttling valves:** any kind of flow-restricting devices that cause a significant pressure drop in the fluid.

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Origin of cooling

- ▶ The magnitude of the temperature drop (or, sometimes, rise) during a throttling process is governed by the Joule- Thomson coefficient.
- ▶ Throttling valves are usually **small devices**, and the flow through them may be assumed to be **adiabatic** ($Q \approx 0$) since there is neither sufficient time nor large enough area for any effective heat transfer to take place.
- ▶ However, **no work** is provided to force the expansion to occur. **Hence**, the energy required to overcome intermolecular forces between gas's molecules are taken from the **internal energy of the gas**. That inspires a temperature drop with expansion.

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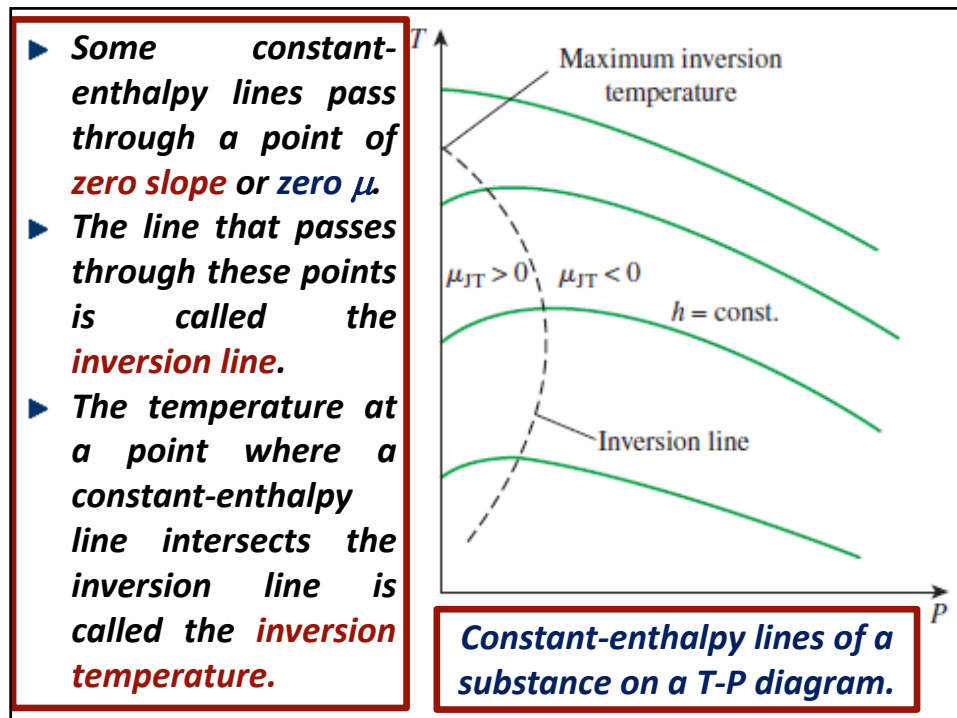
Inversion temperature

- ▶ The temperature above which the expanded gas suffers heating instead of cooling.
- ▶ A fluid may experience a **large drop or increase** in its temperature as a result of throttling.

The temperature behavior of a fluid during a throttling ($H = \text{constant}$) process is described by the **Joule-Thomson coefficient**, defined as

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H \quad \left\{ \begin{array}{l} < 0, T \text{ increases} \\ = 0, T \text{ remains constant} \\ > 0, T \text{ decreases} \end{array} \right.$$

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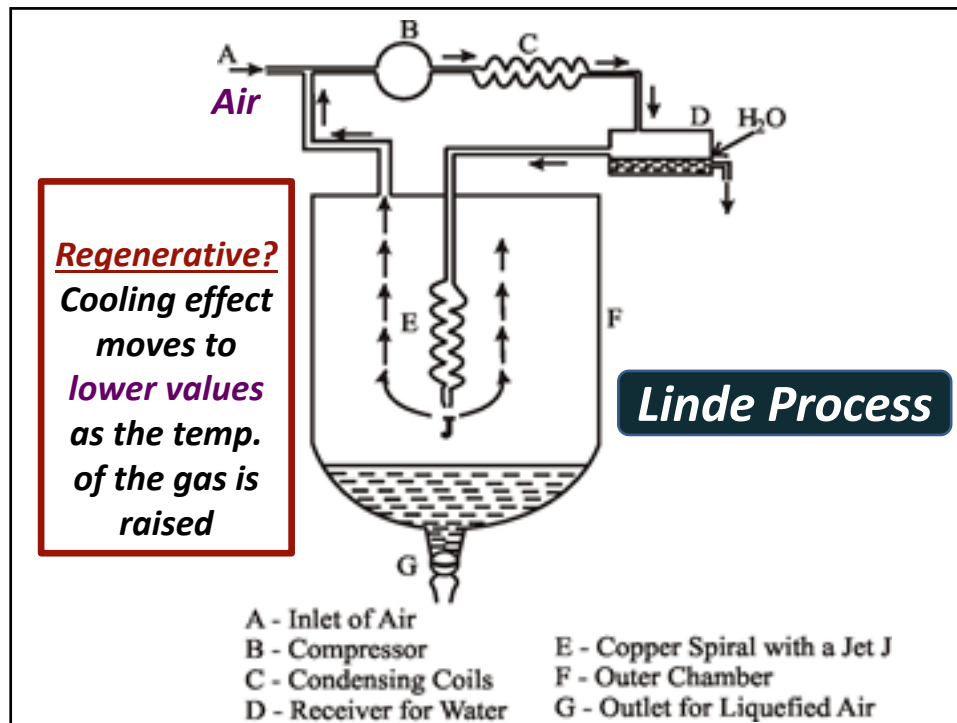
Linde Process (1842–1934)

Liquefaction of air

Joule-Thomson effect
1st principal of liquefaction

- ✦ Air is freed of **carbon dioxide** (passing over **Caustic soda**) and **water** and compressed to **150 -200 atm**.
- ✦ The compressed gas is passed through a copper coil to an expansion nozzle within a Dewar flask.
- ✦ The emerging air is cooled while expanding and then passes back within a second copper coil that surrounds the first coil. Thus the expanded gas cools the incoming gas in a process that is said to be **regenerative**.
- ✦ **Eventually** the air is reduced to its critical temperature and, at the pressure of 150-200 atm (**well above its critical pressure**), liquefies.

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Liquefaction of gases

1 – External work

✚ The 2nd principal of liquefaction (cooling) proceeds by forcing the gas to perform external work adiabatically (under insulation, no heat transfer). Work will be done on the expense of internal energy of the gas.

Liquefaction of air

Claude Process

✚ When a gas expands adiabatically against a piston in an engine, it does some external work, hence its internal energy falls and consequently the temperature of the gas falls.

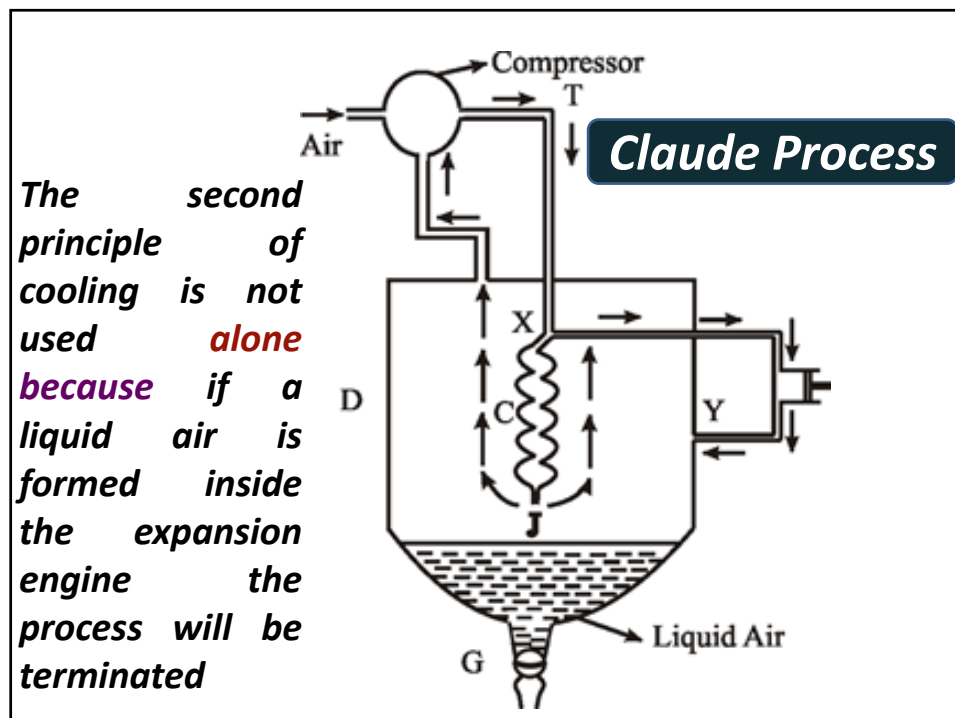
✚ This principle combined with Joule-Thomson effect, has been applied in Claude's process for liquefaction of air.

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Claude Process

- ✚ The purified air (free from CO_2 and water vapors) is first compressed to ca. 200 atm by a compressor then splits:
 - 🌱 Part into a cylinder fitted with an air tight piston
 - ✓ This air pushes the piston and thus does some external work. As a result, the internal energy of air falls and hence temperature falls. The cooled air then enters the chamber at lower end.
 - 🌱 Part passes through a spiral coil which ends in a jet.
 - ✓ This air is cooled by Joule-Thomson effect as it comes out through the jet in low pressure region (50 atm) of chamber. The cooled air is circulated again and again with the incoming air till the air gets liquefied.
- ✚ The liquefied air collects in the chamber and is withdrawn.

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