

Ideal gases (Equation of State)

Non-Ideal/Real gases (Equation of State)

Cubic Equations of State

Many Slides taken from Internet:  
Prof. Cris Cramer, University of Minnesota

## **Ideal gas Equation of State**

## Why GASES ??

Dilute nature permit to establish relationship  
between “**TEMPERATURE, PRESSURE, VOLUME**”

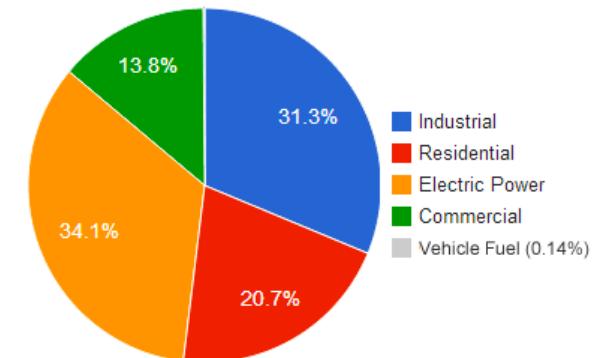


Key principles of ‘Thermodynamic’

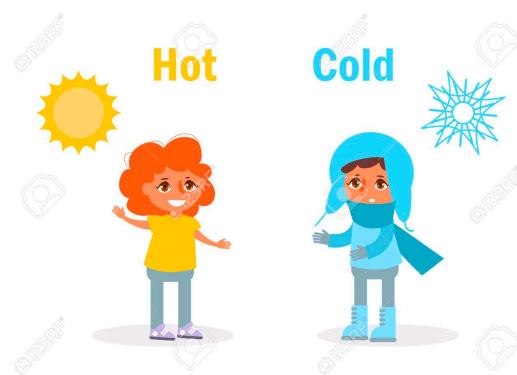


Study reveals apparent ‘Laws’

## Why GASES ??



USA (year 2013)



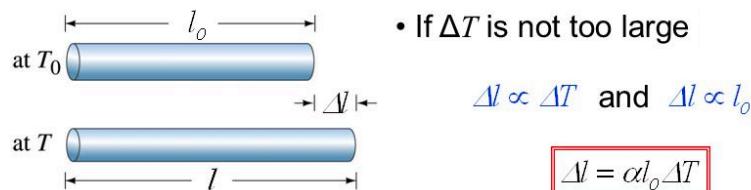
# “Temperature”

Notion of Hot and Cold.  
Don't exactly know how to measure ?

## (1) How to measure ?

### Linear expansion

- Consider a thin rod of initial length,  $l_0$  at temperature,  $T_0$  is heated to a new uniform temperature,  $T$  and acquires length,  $l$  as shown in figure below.

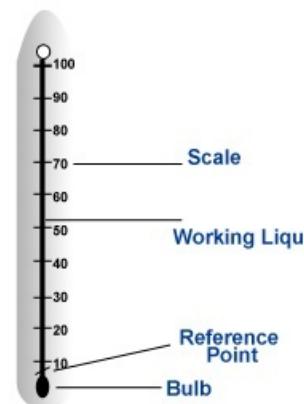


$$\begin{aligned}\Delta l &: \text{change in length} = l - l_0 \\ \Delta T &: \text{change in temperature} = T - T_0 \\ \alpha &: \text{coefficient of linear expansion}\end{aligned}$$

## (2) How to measure ?

Liquid also expand

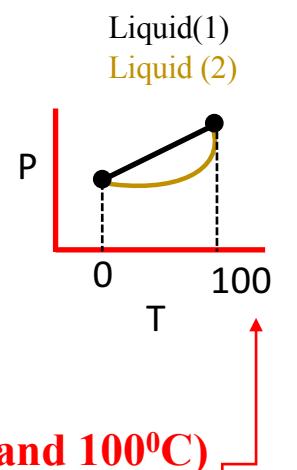
Liquid-in-glass Thermometer



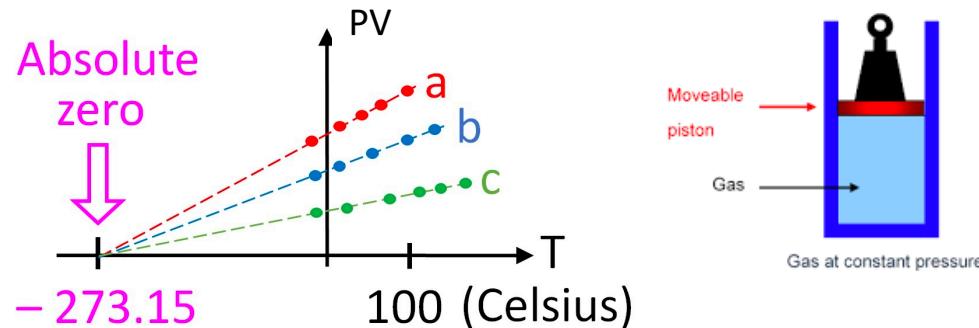
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### Problems

- $H_2O$  ( $T = 0^\circ C$  and  $100^\circ C$ )  
Not unique.
- Variation with temp depends on the nature of the liquid.



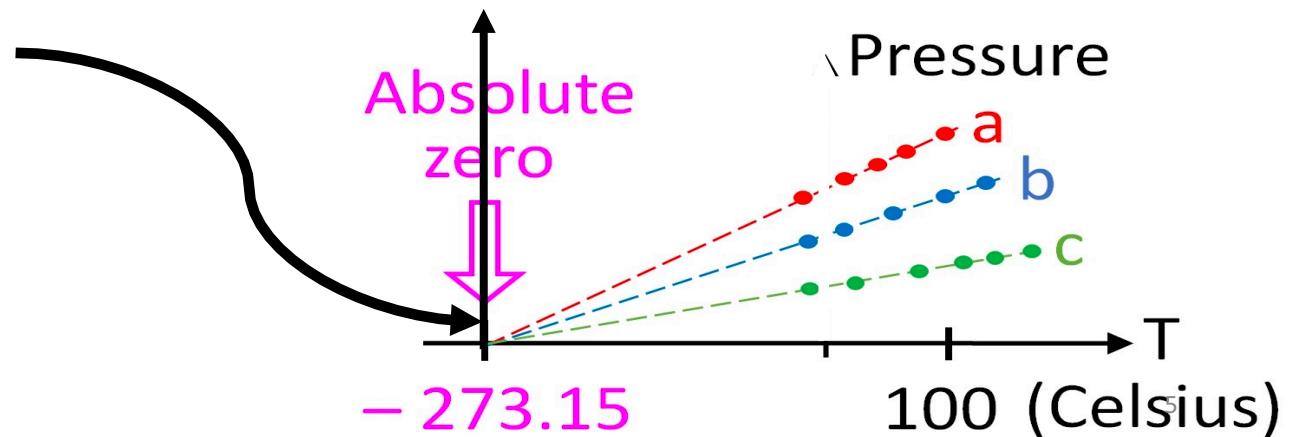
(3) How to measure ?  
GASES also expand

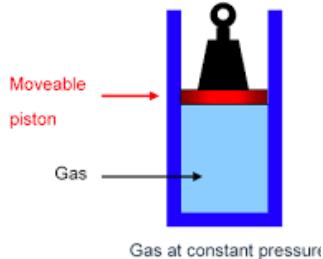


**FOR VERY DILUTE GASES (a, b, c)**

- $PV \propto T$
- $PV = 0$  at absolute zero ( $-273.15^{\circ}\text{C}$ ). No further cooling possible  
( $PV$  cannot be negative)
- New Temperature scale (KELVIN SCALE)

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





## IDEAL GAS EQUATION OF STATE

An *equation of state* details the mathematical relationship between the physical observables *pressure* ( $P$ ), *volume* ( $V$ ), and *temperature* ( $T$ )

The Ideal Gas obeys:  $PV = nRT$       or       $P\bar{V} = RT$ ,  $\bar{V} = \frac{V}{n}$

$\uparrow$      $\uparrow$   
*universal gas constant*                            *molar volume*

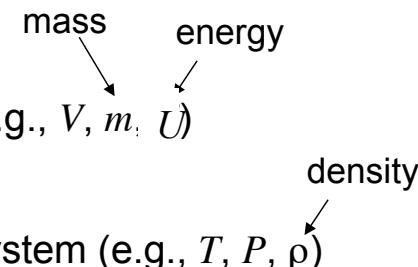
Some definitions:

**extensive variable**

- depends on the size of the system (e.g.,  $V$ ,  $m$ ,  $U$ )

**intensive variable**

- does *not* depend on the size of the system (e.g.,  $T$ ,  $P$ ,  $\rho$ )



## OBSERVED IDEAL GAS “LAWS”

$$PV = nRT \quad \text{or} \quad P\bar{V} = RT, \bar{V} = \frac{V}{n}$$

At constant  $T$ , the product of  $P$  and  $\bar{V}$  must be constant (**Boyle's Law**)

$$P_1\bar{V}_1 = P_2\bar{V}_2 \quad (\text{constant } T)$$

At constant  $P$ , the ratio of  $\bar{V}$  and  $T$  must be constant (**Charles' Law**)

$$\frac{\bar{V}_1}{T_1} = \frac{\bar{V}_2}{T_2} \quad (\text{constant } P)$$

At constant  $V,n$  the ratio of  $P$  and  $T$  must be constant (**Amonton's Law**)

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (\text{constant } V,n)$$

At constant  $P,T$  the ratio of  $V$  and  $n$  must be constant (**Avogadro's Law**)

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (\text{constant } P,T)$$

## TEMPERATURE AND THE GAS CONSTANT

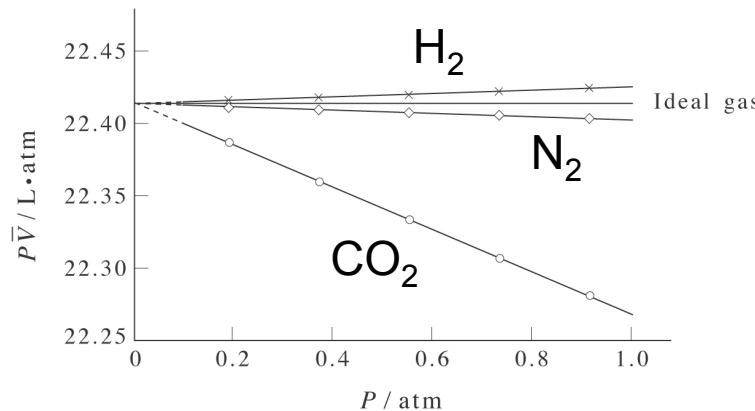
Determination of universal gas constant:  $R = \lim_{P \rightarrow 0} \frac{\bar{PV}}{T}$

0.082058 L•atm•mol<sup>-1</sup>•K<sup>-1</sup>  
0.083145 L•bar•mol<sup>-1</sup>•K<sup>-1</sup>  
83.145 cm<sup>3</sup>•bar•mol<sup>-1</sup>•K<sup>-1</sup>  
8.3145 J•mol<sup>-1</sup>•K<sup>-1</sup>

273.15 K measurements →

At low pressures, *all* gases converge to ideal behavior

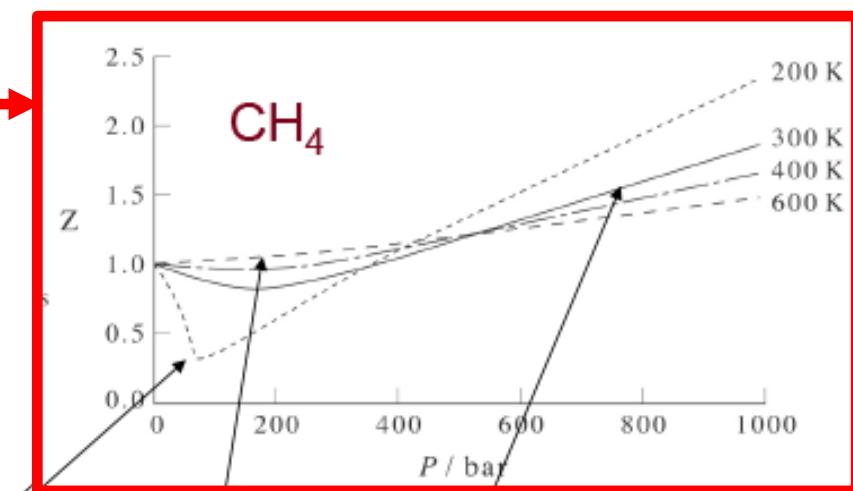
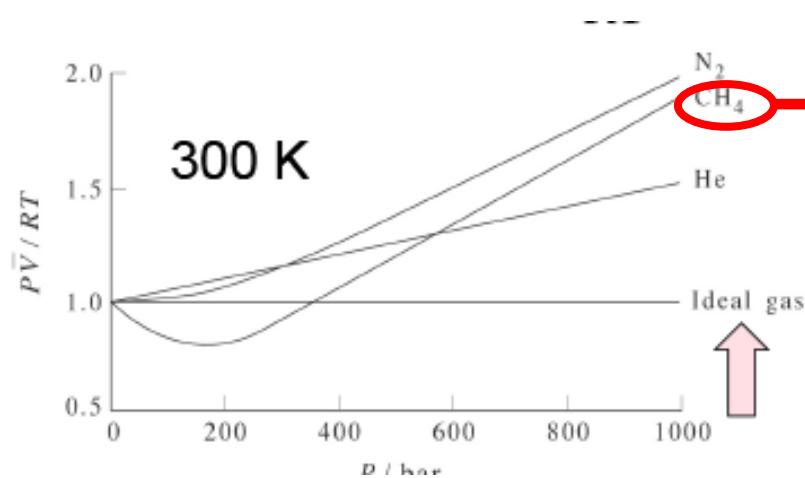
$$\bar{PV}(273.15) = 22.414 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1}$$



## **Non-Ideal gas Equation of State**

## GASES ARE RARELY IDEAL

$$\frac{PV}{RT} = Z \quad \text{compressibility (unitless)}$$



Low  $T$  and low  $P$ : attractive forces

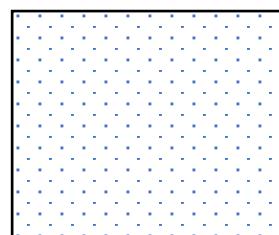
$$\bar{V}_{\text{real}} < \bar{V}_{\text{ideal}}$$

High  $T$  or high  $P$ : repulsive forces

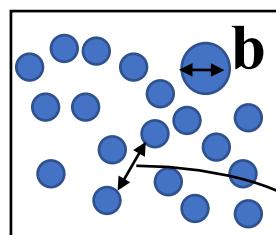
$$\bar{V}_{\text{real}} > \bar{V}_{\text{ideal}}$$

$$PV = nRT$$

(Ideal gas)



Real gas



1. Molecular size :

$$V_{\text{ideal}} = V_{\text{actual}} - nb$$

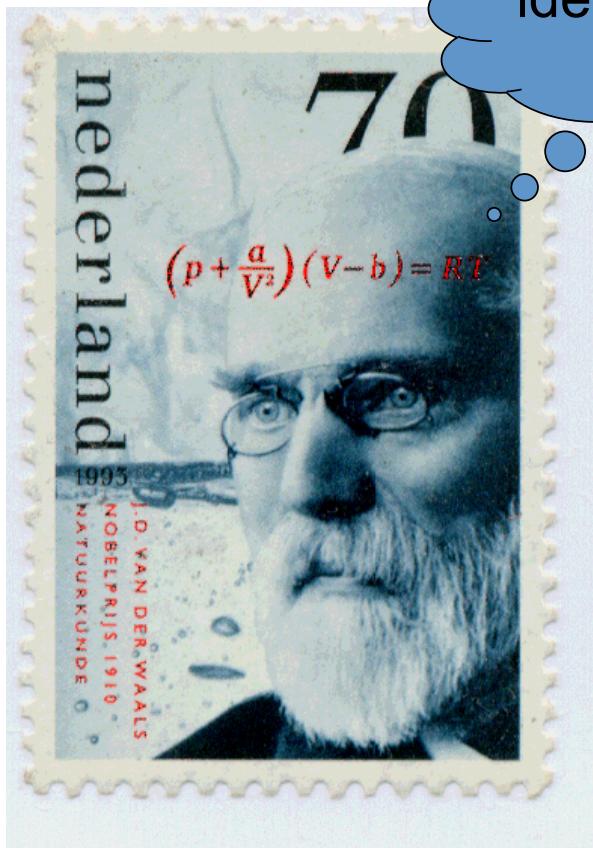
2. Attractive forces:

$$P_{\text{actual}} = P_{\text{ideal}} - \text{CONST}$$

$$\underbrace{P + a \left( \frac{n}{V} \right)^2}_{\text{ideal gas pressure}} \times \underbrace{(V - nb)}_{\text{ideal gas volume}} = nRT$$

$$\begin{aligned} &\propto (n/V) * (n/V) \\ &\propto (n/V)^2 \\ &= a \cdot (n/V)^2 \end{aligned}$$

# JOHANNES DIDERIK VAN DER WAALS



ideal nonsense!

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

*van der Waals equation of state*

*a* and *b* are constants that depend on the specific gas in question:

*a* ~ intermolecular interaction strength  
*b* ~ molecular size

	<i>a</i> (dm <sup>6</sup> •bar•mol <sup>-2</sup> )	<i>b</i> (dm <sup>3</sup> •mol <sup>-1</sup> )
helium	0.035	0.024
ammonia	4.304	0.037

# VDW Equation of State and Experiment

$$(P + \frac{a}{V^2})(V - b) = RT$$

① Low pressure region  
volume is large  $V \gg b$

$$\therefore \left( P + \frac{a}{V^2} \right) V = RT$$

$$\Rightarrow \frac{PV}{RT} = 1 - \frac{a}{VRT}$$

$$\Rightarrow Z = 1 - \frac{a}{VRT}$$

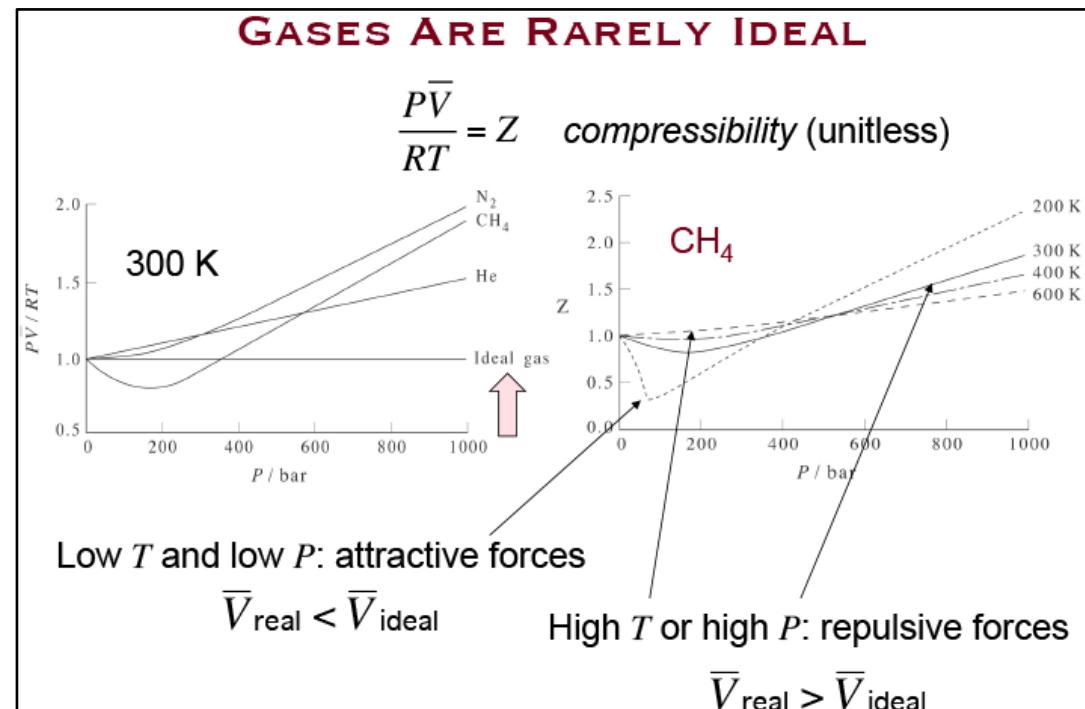
$Z < 1$  at low pressure

② High pressure region  
 $V$  is small,  $P > \frac{a}{V^2}$

$$P(V-b) = RT$$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$Z > 1$  at high pressure



(3) Eqn 1: At very low pressure (Large  $V$ ) and High temp (Neglect  $a/VRT$ )  
 $PV = RT$

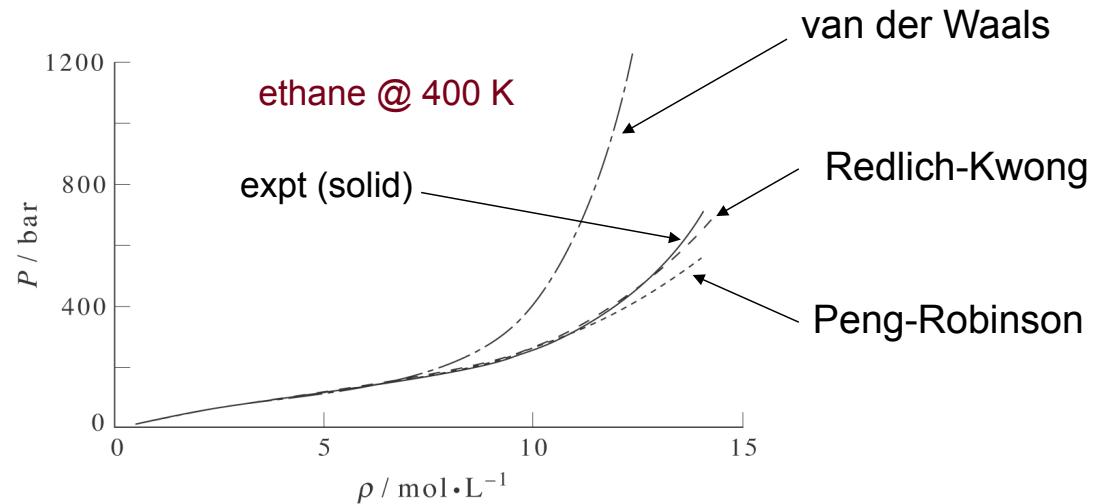
## VARIOUS CUBIC EQUATIONS OF STATE

van der Waals 
$$P = \left( \frac{RT}{\bar{V} - b} \right) - \left( \frac{a}{\bar{V}^2} \right)$$

Redlich-Kwong 
$$P = \left( \frac{RT}{\bar{V} - B} \right) - \left( \frac{A}{T^{1/2} \bar{V} (\bar{V} + B)} \right)$$

Peng-Robinson 
$$P = \left( \frac{RT}{\bar{V} - \beta} \right) - \left( \frac{\alpha}{\bar{V}(\bar{V} + \beta) + \beta(\bar{V} - \beta)} \right)$$

## VARIOUS CUBIC EQUATIONS OF STATE



Improved performance of the  
more complex equations of state  
at very high pressures

$$\bar{V}^{-1} = \rho \quad (\text{mol} \cdot \text{L}^{-1})$$

$$1 \text{ L} = 1 \text{ dm}^3$$



**Next (L2):**  
**Gas-Liquid PV diagram**  
**Law of Corresponding States**