Attempts to describe the behavior of real gases

- The virial equation and the van der Waals equation both attempt to describe the behavior of real gases, accounting for deviations from ideal gas behavior.
- virial equation of state:
 - Derived from statistical mechanics
 - Provides a good fit for experimental data over a wide range of conditions, particularly at low to moderate densities.
- van der Waals equation:
 - Empirical with physical basis Introduces two parameters (a and b) to approximate real gas behavior.
 - Simpler: Requires only two parameters, a and b, which can be determined experimentally.

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Constants a and b are called the van der Waals coefficients

a => strength of attractive interactions

b => strength of repulsive interactions

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	$a/(atm dm^6 mol^{-2})$	$b/(10^{-2}\mathrm{dm^{3}mol^{-1}})$
Ar	1.337	3.20
CO ₂	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

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The loop does not correspond to physical reality but rather reflects the equation's limitations in describing phase transitions accurately.

This region represents the coexistence of liquid and gas phases during the phase transition.

van der Waals parameters and critical constants

$$V_{\rm c} = 3b$$
 $p_{\rm c} = \frac{a}{27b^2}$ $T_{\rm c} = \frac{8a}{27bR}$

- The critical point is the condition where the difference between liquid and gas phases disappears, occurring at specific values of pressure (Pc), temperature (Tc), and molar volume (Vc).
- The critical constants (Pc, Vc, and Tc) are related to the van der Waals parameters (a and b) because these parameters describe the interactions between molecules and their sizes.

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The **van der Waals equation** predicts a critical compression factor of:

$$Z_{\rm c} = \frac{p_{\rm c}V_{\rm c}}{RT_{\rm c}} = \frac{3}{8}$$

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Equations of state

	Equation
Perfect gas	$p = \frac{nRT}{V}$
van der Waals	$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$
Berthelot	$p = \frac{nRT}{V - nb} - \frac{n^2a}{TV^2}$
Dieterici	$p = \frac{nRTe^{-na/RTV}}{V - nb}$

Virial equation of state

$$pV_{\rm m} = RT(1 + B'p + C'p^2 + \cdots)$$

$$pV_{\rm m} = RT \left(1 + \frac{B}{V_{\rm m}} + \frac{C}{V_{\rm m}^2} + \cdots \right)$$

Reduced variables



- State variables scaled by the properties at its critical point
- Dimensionless

CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 16: Molecules in motion

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics

Focus 19: Processes at solid surfaces

Focus 2: The First Law

Internal Energy

Enthalpy

Thermochemistry

State functions

Adiabatic changes

Thermodynamics is the study of the transformations of energy

Systems and surroundings

Systems and surroundings



- **Energy:** The capacity to do work or transfer heat. It exists in various forms, such as kinetic, potential, internal, chemical, etc.
- Work: Energy transfer that occurs when a force is applied over a distance or a system changes (e.g., compression of a gas, moving a piston). It is organized energy transfer.
- Heat: Energy transfer due to a temperature difference between a system and its surroundings. It is disorganized energy transfer associated with random molecular motion.









Diathermic wall (passage of heat is permitted)









Diathermic wall (passage of heat is permitted)

work
$$1 J = 1 N m = 1 kg m^2 s^{-2}$$





(passage of heat not permitted)



Diathermic wall (passage of heat is permitted)





Exothermic vs endothermic

Exothermic vs endothermic



Exothermic vs endothermic



 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

 $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$

The molecular interpretation of heat and work

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Energy

The molecular interpretation of heat and work



Heat

Work

Energy



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Units: J

 $U_m = U/n \Rightarrow$ intensive (J/mol)