



**Sharif University of Technology
School of Mechanical Engineering
Center of Excellence in Energy Conversion**

Advanced Thermodynamics

Lecture 21

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Van der Waal's Equation of State

Good only for moderate to low pressures

$$p = \frac{R_u T}{\bar{v} - b} - \frac{a}{\bar{v}^2} \quad \text{or} \quad p = \frac{nR_u T}{\bar{v} - nb} - \frac{n^2 a}{\bar{v}^2} \quad \text{if there are } n \text{ moles of gas}$$

Van der Waals Constants

Substance	a Liters-atm/mole	b Liters/mole
Methane	2.253	0.04278
Ethane	5.489	0.06380
Propane	8.664	0.08445
Isobutane	12.87	0.1142
<i>n</i> -Butane	14.47	0.1226
Isopentane	18.05	0.1417
<i>n</i> -Pentane	19.01	0.1460
<i>n</i> -Hexane	24.39	0.1735
<i>n</i> -Heptane	31.51	0.2654
Nitrogen	1.390	0.03913
Carbon dioxide	3.592	0.04267
Hydrogen sulfide	4.431	0.04267
Helium	0.03412	0.02370
Water	5.464	0.03049
Hydrogen	0.2444	0.02661
Ethylene	4.471	0.05714
Propylene	8.379	0.08272

*This heading is incorrect!
It should be:*

$$\frac{\text{liter}^2 - \text{atm}}{\text{mole}^2}$$

Approximations for a & b

$$a = 3p_{pc}V_{pc}^2$$

$$b = \frac{V_{pc}}{3}$$

$$\text{Ideal Gas: } \bar{v} = \frac{\bar{R}T}{P} \qquad \text{V.D.W: } P = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

∅ Other form of V.D.W Eq.:

$$P\bar{v} = \bar{R}T + \bar{R}T \frac{b - a}{\bar{v}} + \bar{R}T \frac{b^2}{\bar{v}^2} + \bar{R}T \frac{b^3}{\bar{v}^3} + \dots$$

$$\left(\frac{\partial P}{\partial \bar{v}} \right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \bar{v}^2} \right)_{T_c} = 0$$

$$\rightarrow v_c = 3bP_c = \frac{a}{27b^2} T_c = \frac{8a}{27Rb}$$

$$Z_c = \frac{P_c v_c}{RT_c} = 0.375$$

It is unreal value, generally $0.23 < Z_c < 0.33$

Benedict-Webb-Rubin Equation of State

Applicability:

- *Above and below critical pressure*
- *Light hydrocarbons (generally natural gas)*
- *Single and 2-phase regions*

$$p = RT\bar{\rho} + (B_0R_uT - A_0 - C_0/T^2) + (bR_uT - a)\bar{\rho}^3 + a\alpha\bar{\rho}^6 + \frac{c\bar{\rho}^3}{T^2} \left[(1 + \gamma\bar{\rho}^2)e^{(-\gamma\bar{\rho}^2)} \right]$$

$$\bar{\rho} = \text{molar density} = 1/\bar{v} = \rho/M = \frac{1}{\bar{v}M} \left(\frac{\text{lbmol}}{\text{ft}^3} \right)$$

B-W-R Constants

Benedict–Webb–Rubin Constants

Substance	A_0	B_0	$C_0 \times 10^{-6}$	a	b	$c \times 10^{-6}$	$\alpha \times 10^3$	$\gamma \times 10^2$
Methane	6,995.25	0.682,401	275.763	2,984.12	0.867,325	498.106	511.172	153.961
Ethane	15,670.7	1.005,54	2,194.27	20,850.2	2.853.93	6,413.14	1,000.44	302.790
Propane	25,915.4	1.558,84	6,209.93	57,248.0	5.773,55	25,247.8	2,495.77	564.524
Isobutane	38,587.4	2.203,29	10,384.7	117,047	10.889,0	55,977.7	4,414.96	872.447
<i>n</i> -Butane	38,029.6	1.992,11	12,130.5	113,705	10.263,6	61,925.6	4,526.93	872.447
Isopentane	4,825.36	2.563,86	21,336.7	226,902	17.144,1	136,025	6,987.77	1,188.07
<i>n</i> -Pentane	45,928.8	2.510,96	25,917.2	246,148	17.144,1	161,306	7,439.92	1,218.86
<i>n</i> -Hexane	5,443.4	2.848,35	40,556.2	429,901	28,003,2	296,077	11,553.9	1,711.15
<i>n</i> -Heptane	66,070.6	3.187,82	57,984.0	626,106	38,991,7	483,427	16,905.6	2,309.42
Nitrogen								
Carbon dioxide								
Hydrogensulfide								
Helium								
Water								
Hydrogen								
Ethylene	12,593.6	0.891,980	1,602.28	15,645.5	2.206,78	4,133.60	731.661	236.844
Propylene	23,049.2	1.362,63	5,365.97	46,758.6	4.799,97	20,083.0	1,873.12	469.325

Units: p =psia, T =°R, molar density=lbmol/ft³

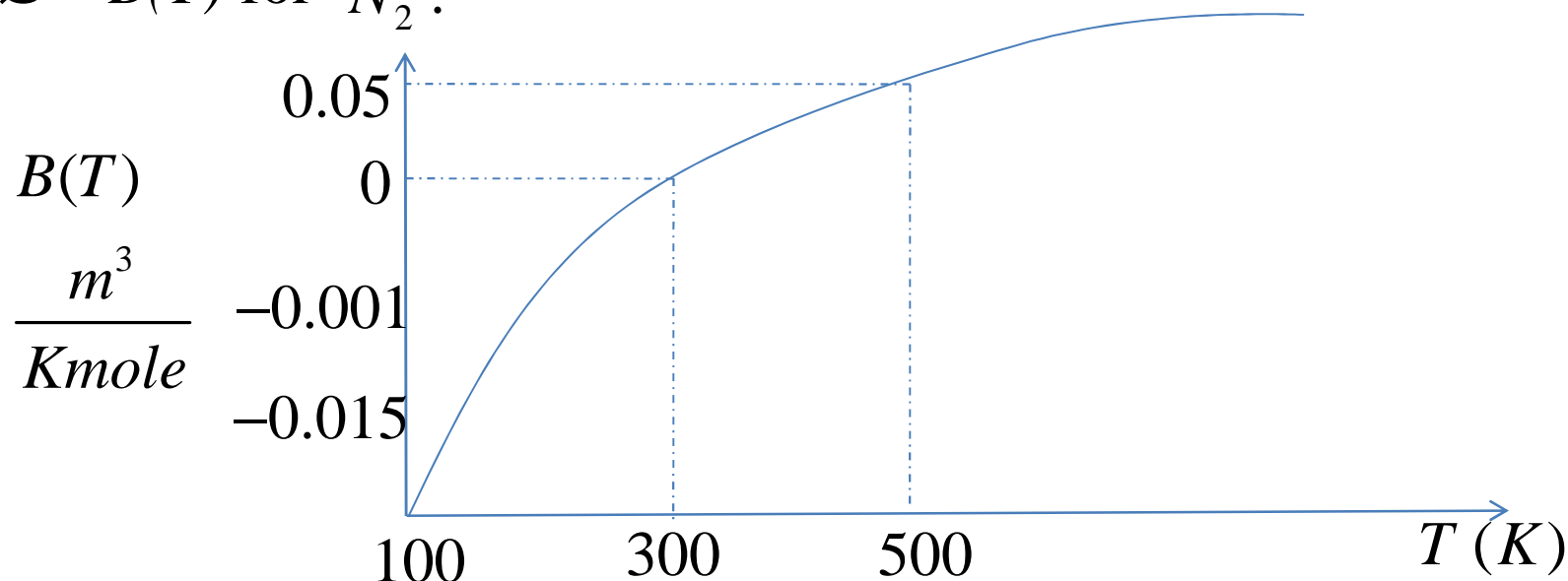
∅ Virial Form:

$$Z = \frac{Pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \dots$$

∅ $B(T)$: First approximation being non-ideal gas, second virial coefficient (consideration of two molecules collision).

∅ $C(T), D(T), \dots$

∅ $B(T)$ for N_2 :



$$Z = \frac{Pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \dots$$

$$\rightarrow v = \frac{RT}{P} + B(T) \frac{RT}{Pv} + C(T) \frac{RT}{Pv^2} + D(T) \frac{RT}{Pv^3} + \dots$$

$$a = \frac{RT}{P} - v$$

$$\lim_{P \rightarrow 0} a = \lim_{P \rightarrow 0} \left(\frac{RT}{P} - v \right) = \lim_{P \rightarrow 0} \left[-B(T) \frac{RT}{Pv} - C(T) \frac{RT}{Pv^2} + \dots \right]$$

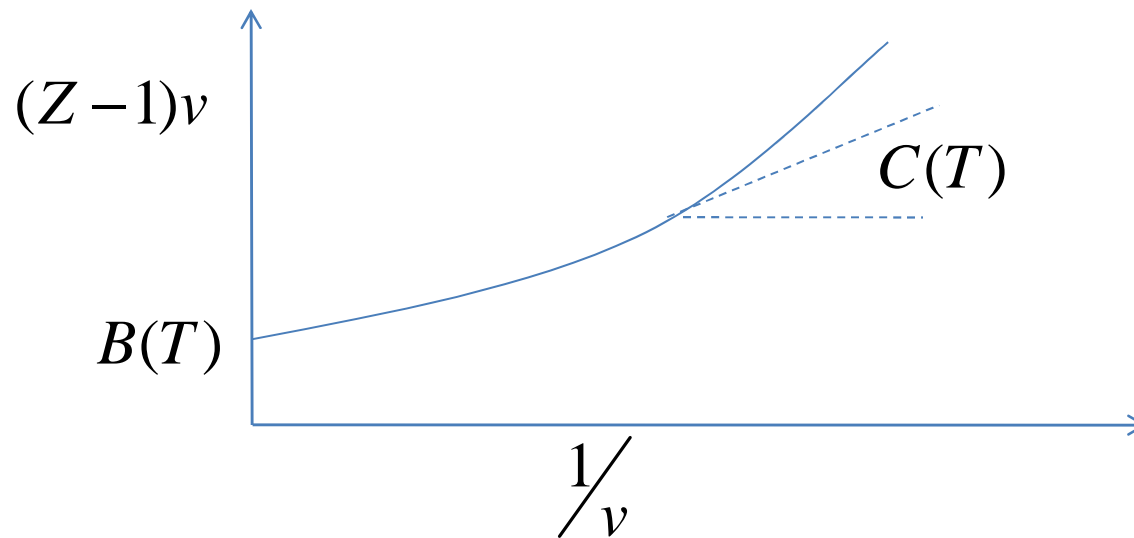
$$\Rightarrow \lim_{P \rightarrow 0} a = -B(T) \rightarrow 0 \text{ at } T = T_{Boyle}$$

∅ $\lim_{P \rightarrow 0} a$ is directly related to $B(T)$ (observed experimentally).

$$\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_{T_r} = \lim_{P \rightarrow 0} \left(\frac{Z-1}{P-0} \right) = -\frac{1}{\bar{RT}} \lim_{P \rightarrow 0} \left(\bar{v} - \frac{\bar{RT}}{P} \right) = -\frac{1}{\bar{RT}} \lim_{P \rightarrow 0} a$$

$$v = \frac{RT}{P} + B(T) \frac{RT}{Pv} + C(T) \frac{RT}{Pv^2} + D(T) \frac{RT}{Pv^3} + \dots$$

$$\rightarrow (Z-1)v = B(T) + C(T) \frac{1}{v} + D(T) \frac{1}{v^2} + \dots$$



$$\emptyset \quad \text{If} \quad Z = \frac{Pv}{RT} = 1 + \frac{B(T)}{v} \quad \rightarrow \bar{v} = \frac{1 \pm \sqrt{1 + 4B(T)P/\bar{RT}}}{2P/\bar{RT}}$$

- ∅ We are looking for potential functions which calculate the forces appeared in the equation of state in virial form.

$$B(T) = -2pN_0 \int_0^\infty \left(e^{\frac{-E(r)}{KT}} - 1 \right) r^2 dr$$

N_0 = Avogadro No. and $E(r)$ = Intermolecular Potentiyal Function

- ∅ It is desired to model $E(r)$ to obtain $B(T)$.
- ∅ It is impossible to integrate the above equation to obtain $B(T)$. However, it is possible to approximate it by a power series.

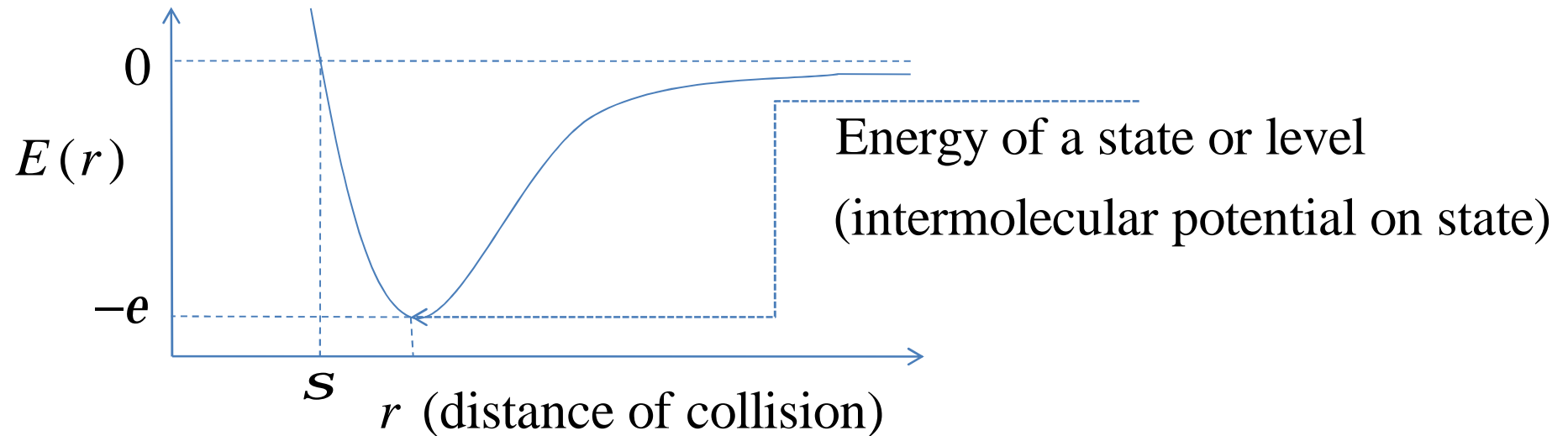
$$B(T) = b_0 \cdot B^*(T^*)$$

$$b_0 = \frac{2}{3} p N_0 \mathcal{S}^3, T^* = \frac{T}{e/K},$$

$B^*(T^*)$ is determined in terms of e/K and b_0

∅ Lenard-Jones [6-12] Model for $E(r)$

$$\frac{E(r)}{RT} = \frac{4e}{RT} \left[\left(\frac{s}{r} \right)^{12} - \left(\frac{s}{r} \right)^6 \right]$$



s = The radial position where $E(r)$ takes zero value

e = A distance denoting the depth of the potential well

∅ The maximum energy of attraction occurs at $r = 2^{1/8} s$