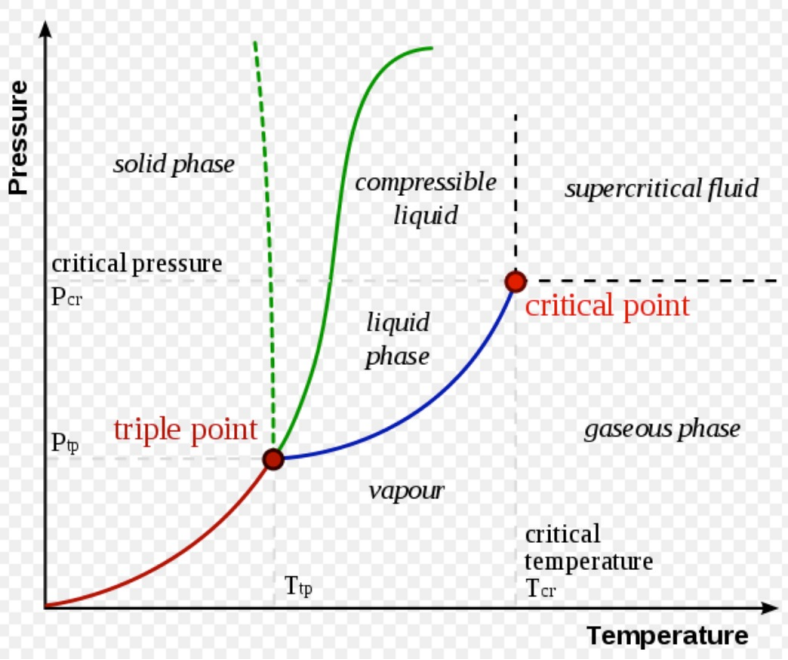
Chemical Engineering Thermodynamics

Lecture 2 The *PVT* Behavior

Xiaofei Xu

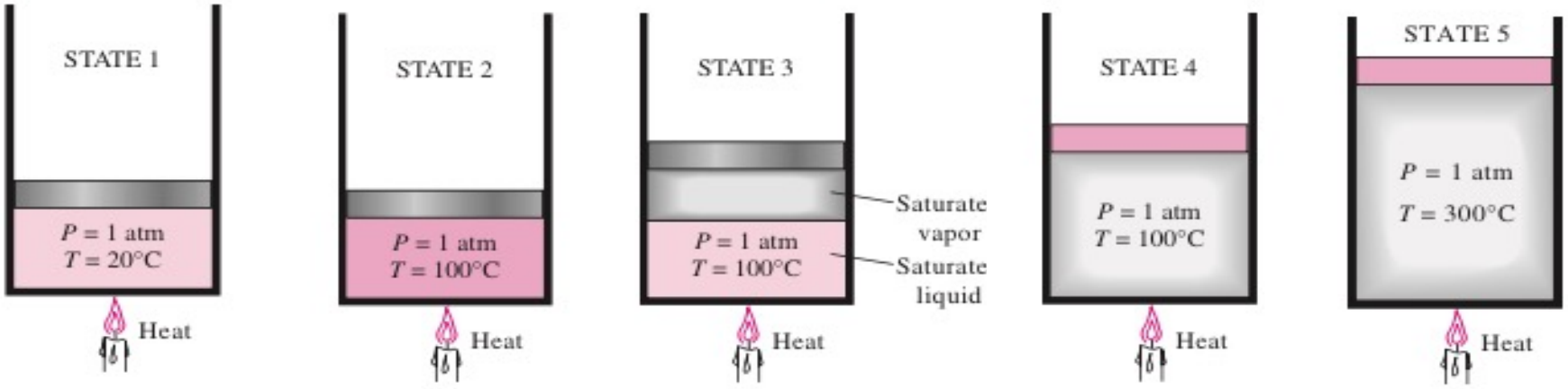


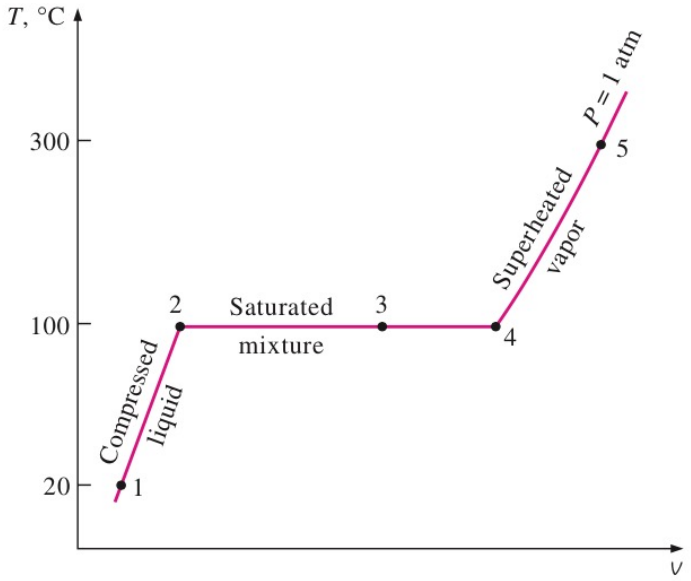
The Phase Rule

$$F = 2 - \pi + N$$

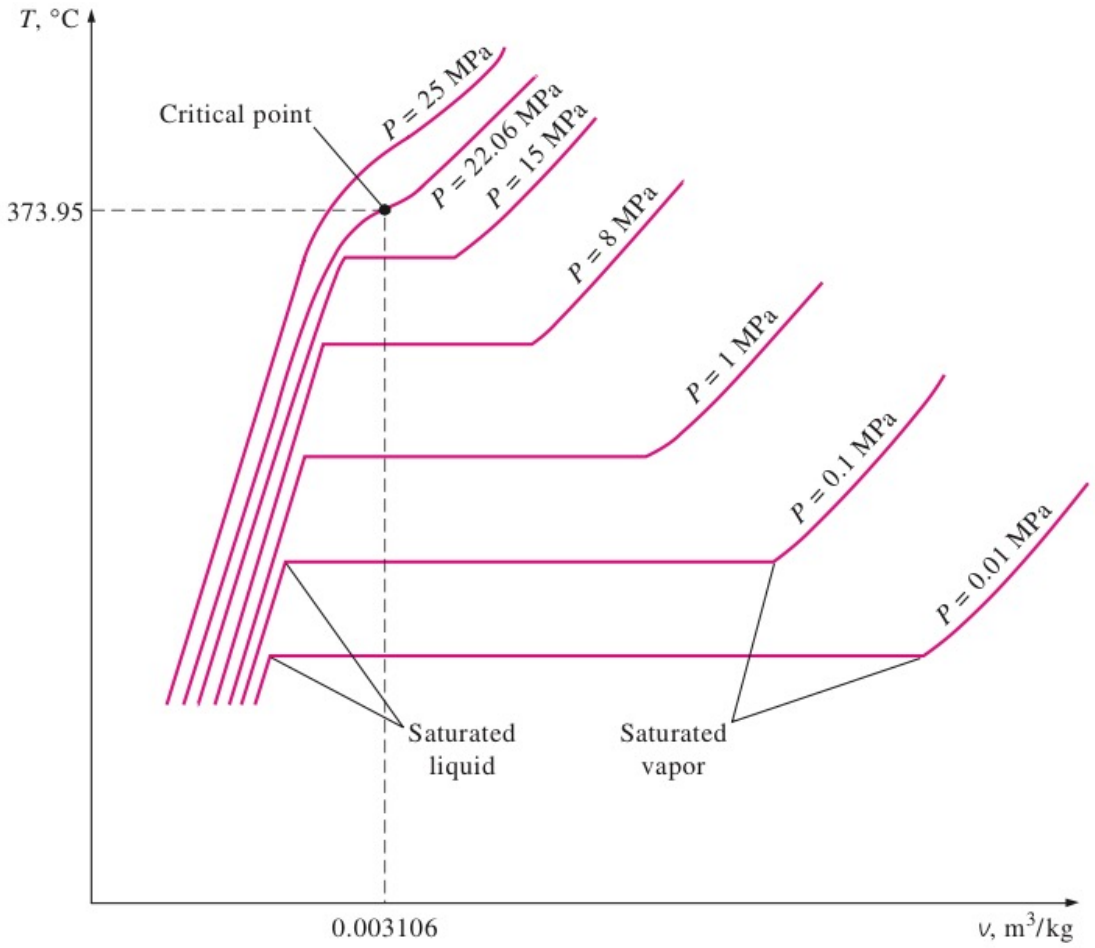
- F: the number of degrees of freedom
- π: the number of phases
- N: the number of species

Liquid-Vapor Phase Transition

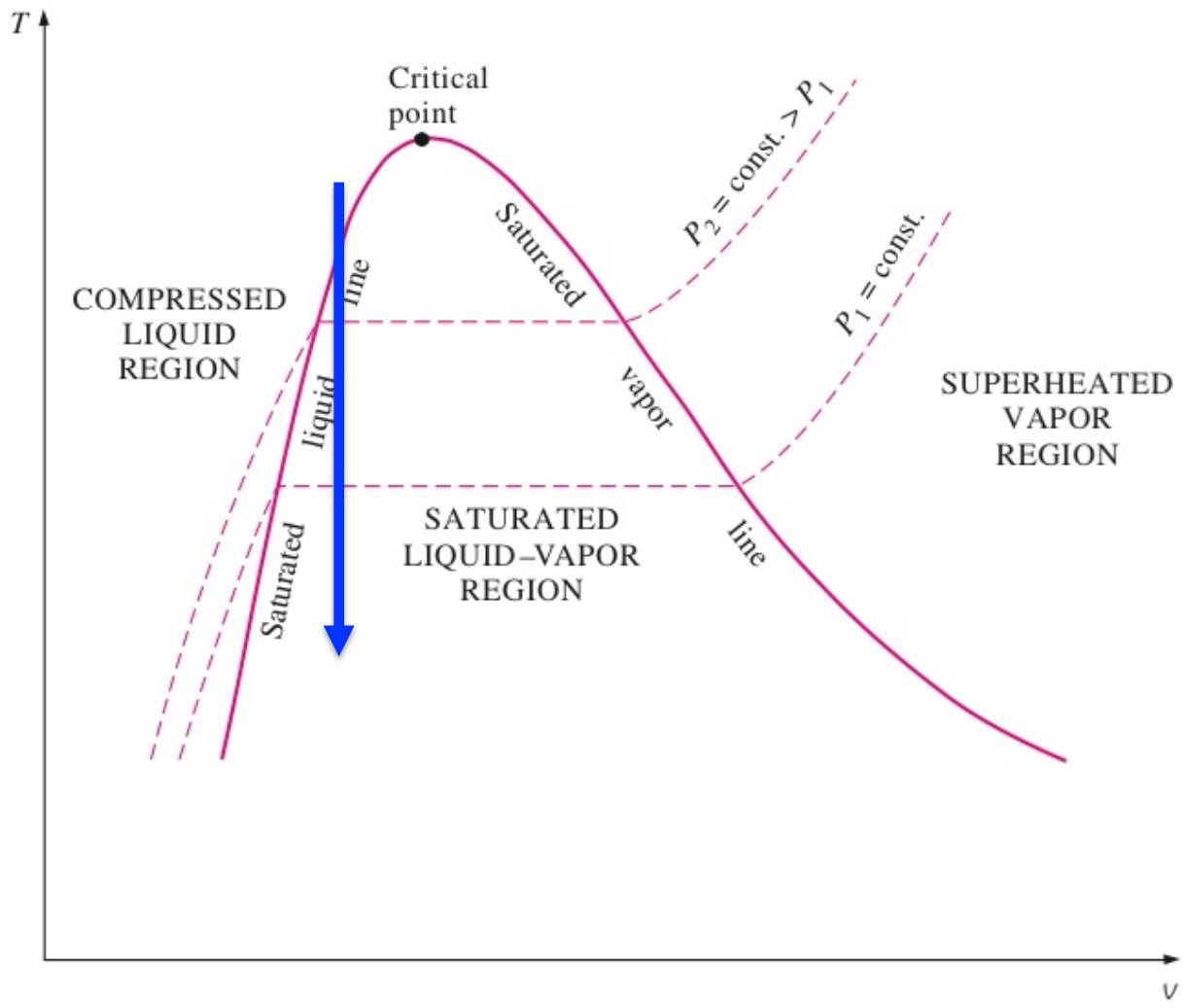




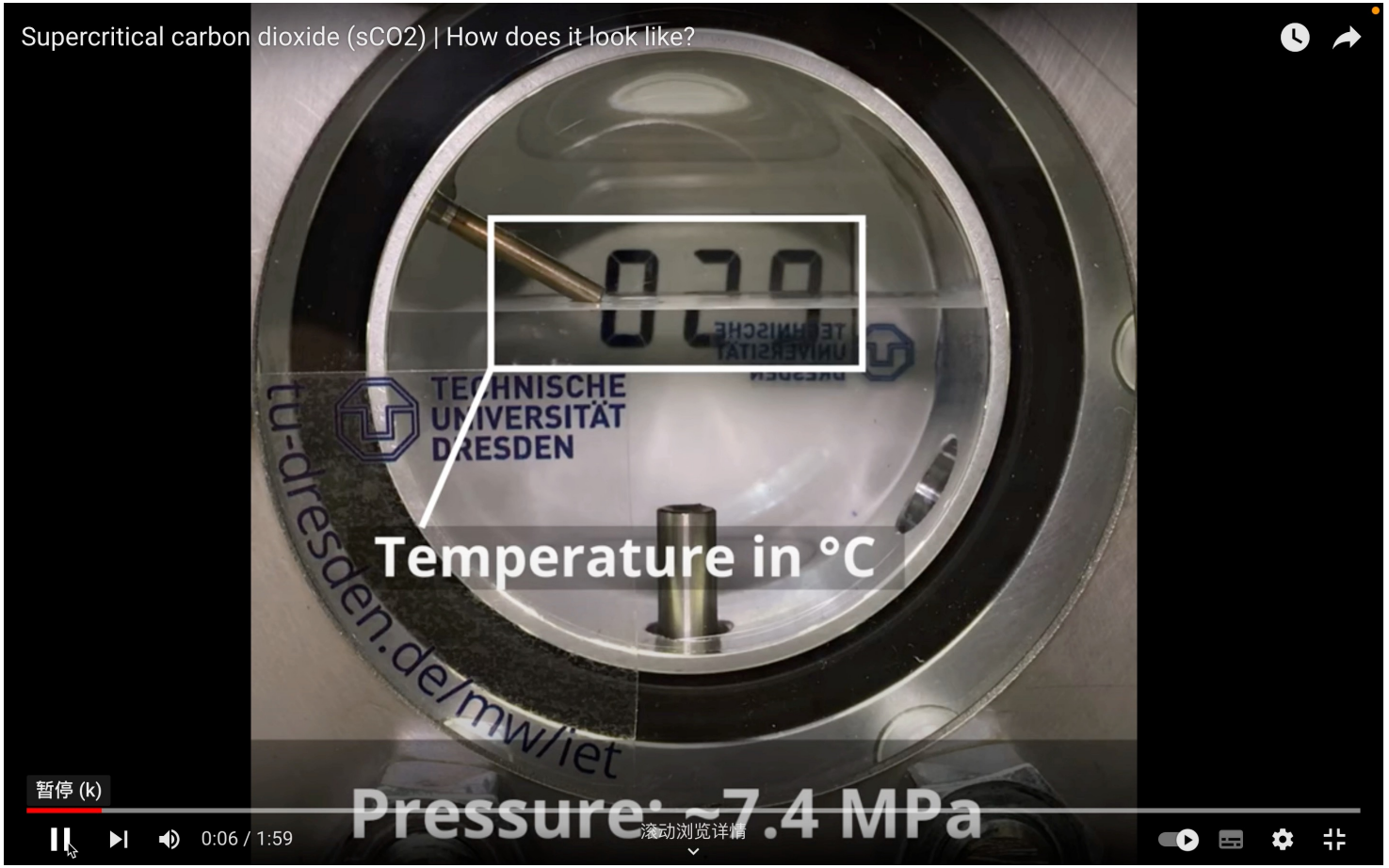
T-V Phase Diagram



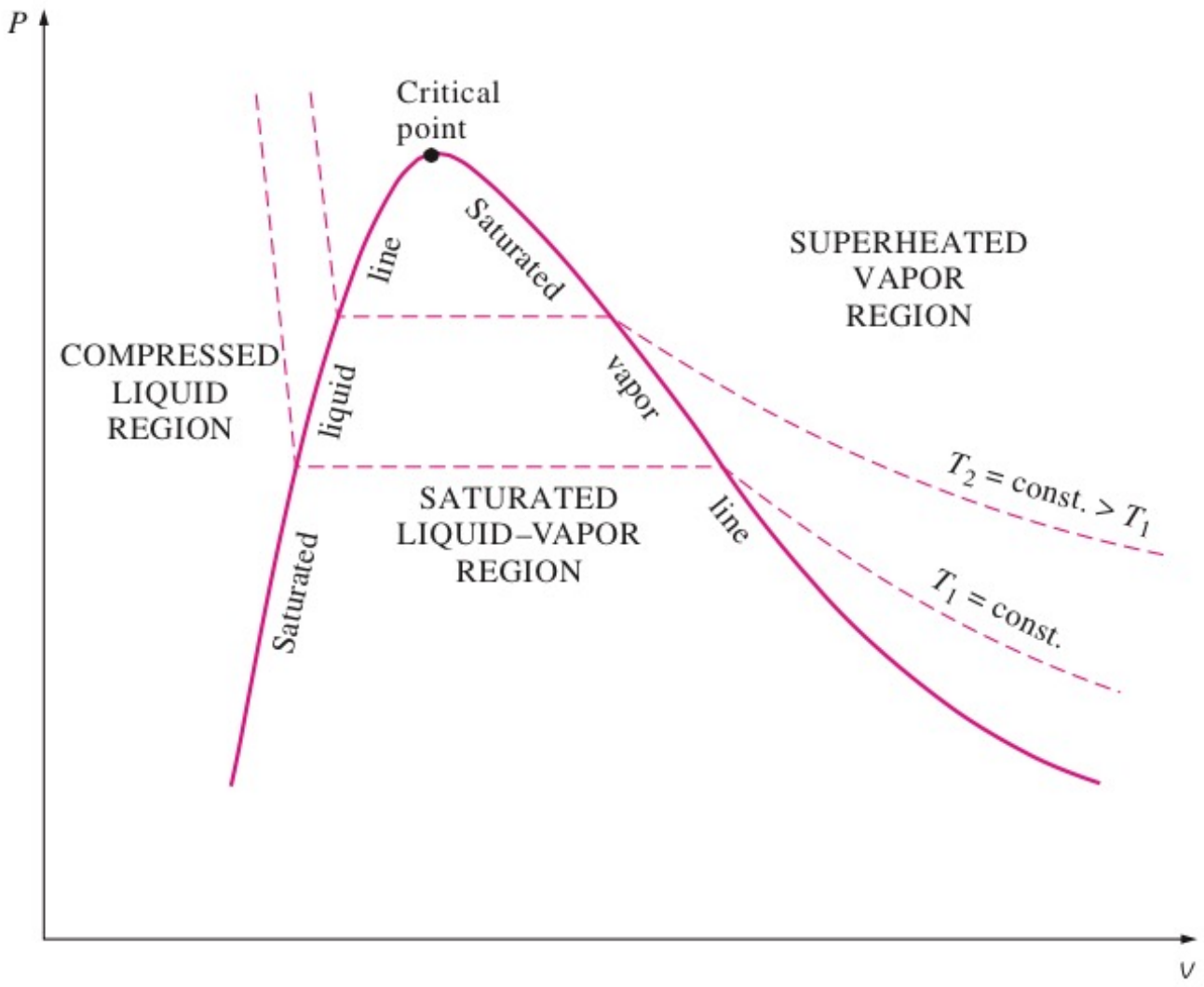
T-V Phase Diagram



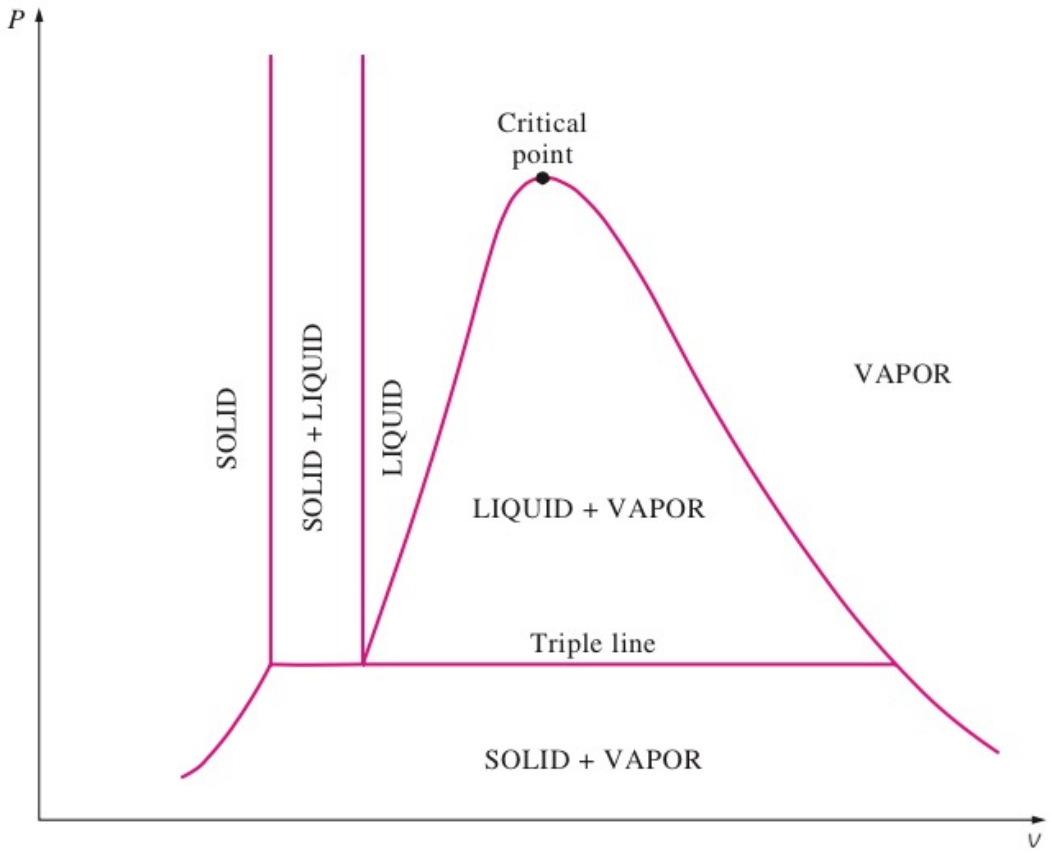
Phase Transition of CO2



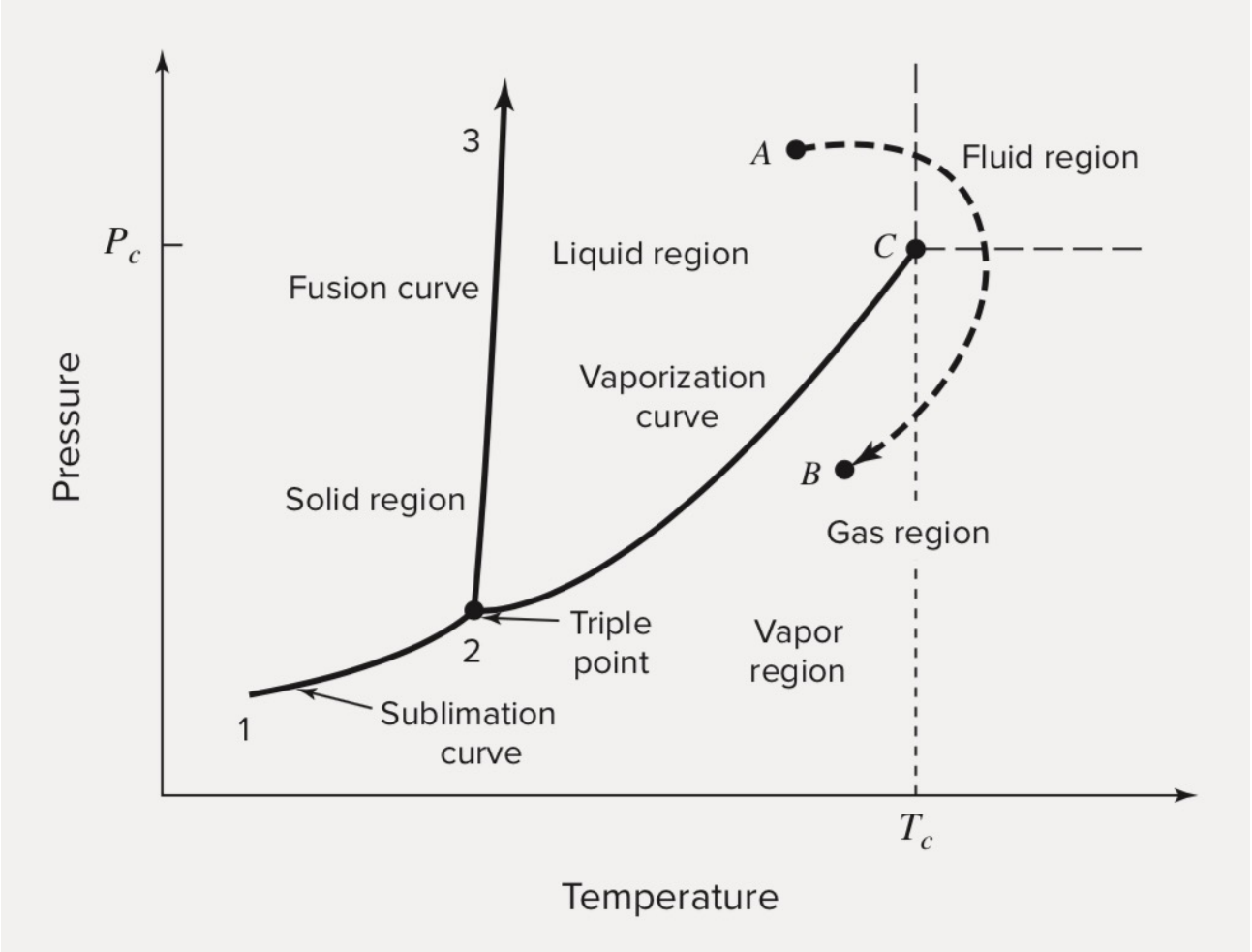
P-V Phase Diagram



Full Phase Diagram



PT Phase Diagram



Compressibility

- Volume expansivity: $\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
- Isothermal compressibility: $\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Example

For liquid acetone at 20°C and 1 bar,

$$\beta = 1.487 \times 10^{-3}\ °C^{-1} \quad \kappa = 62 \times 10^{-6}\ bar^{-1} \quad V = 1.287\ cm^3 \cdot g^{-1}$$

For acetone, find:

(*a*) The value of $(\partial P/\partial T)_V$ at 20°C and 1 bar.

(*b*) The pressure after heating at constant V from 20°C and 1 bar to 30°C.

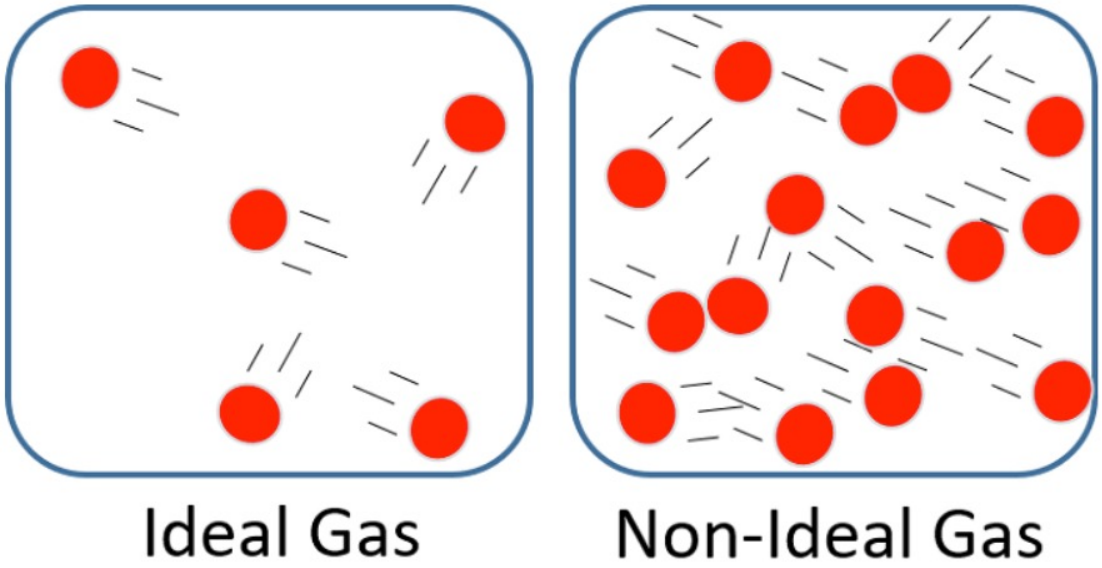
(*c*) The volume change when T and P go from 20°C and 1 bar to 0°C and 10 bar.

$$\frac{dV}{V} = \beta\, dT - \kappa\, dP$$

$$\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

Ideal Gas

- Point particles with no volume
- No interaction; move randomly and independently
- Collide elastically by following Newton's 2nd law



Real gas at high T or low P can be regarded as ideal gas

Ideal-Gas EOS

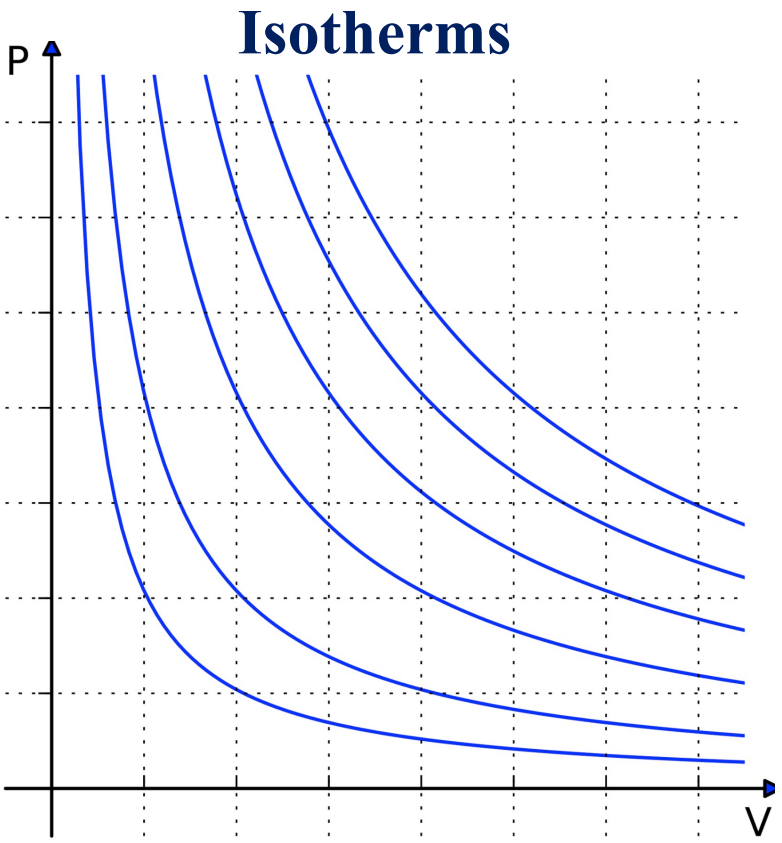
$$PV = nRT$$
$$PV = mR_mT$$
$$PV_n = RT$$
$$PV = NkT$$
$$\rho = \beta P$$

Boltzmann constant

$$k = R / N_A$$
$$= 1.38 \times 10^{-23} J / K$$

Internal Energy and Enthalpy

- Joule's second law
- The internal energy of ideal gas depends only on it temperature



$$U_n \equiv U_n(T)$$
$$dU_n = C_{V,n}dT$$
$$dH_n = C_{p,n}dT$$
$$C_{p,n} = C_{V,n} + R$$

Heat Transfer and Work

Moving boundary work: $dW = PdV$
The first law: $dQ - dW = \mathrm{d}U$
Heat capacity: $dU = nC_{v,n}dT$

Heat: $dQ = nC_{v,n}dT + nRT\frac{dV}{V}$

Work: $dW = nRT\frac{dV}{V}$

Ideal-Gas Process

- Isothermal process

$$Q = W = nRT \ln \frac{V_2}{V_1}$$

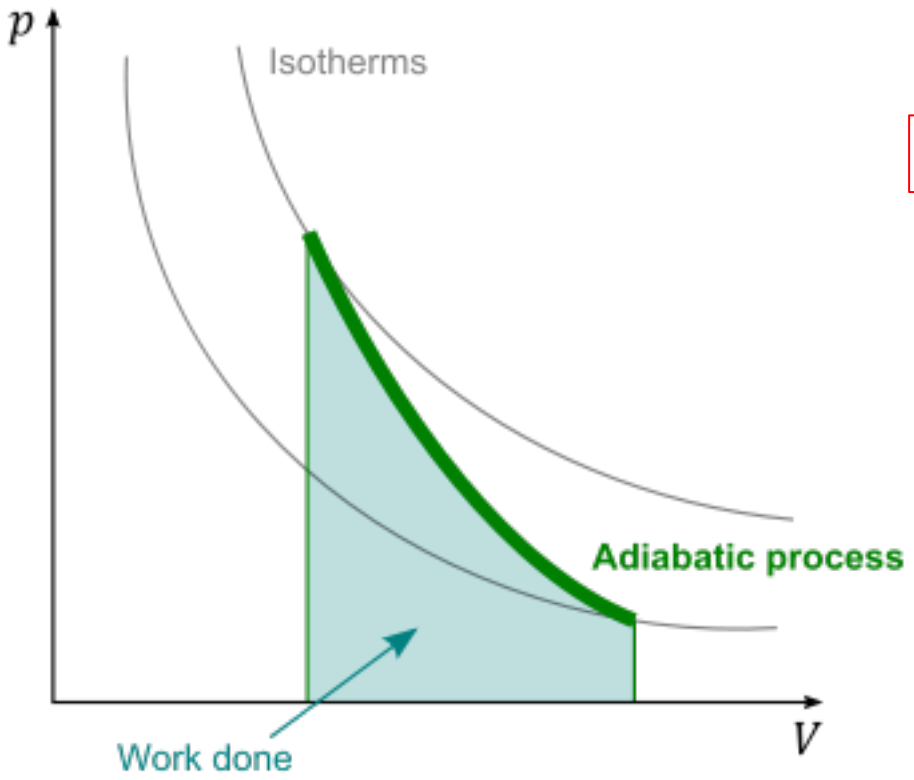
- Isobaric process

$$Q = \Delta H = n \int C_{P,n} dT$$

- Isochoric process

$$Q = \Delta U = n \int C_{V,n} dT$$

Adiabatic Process and Poisson Equation



$$\Delta U = -W$$

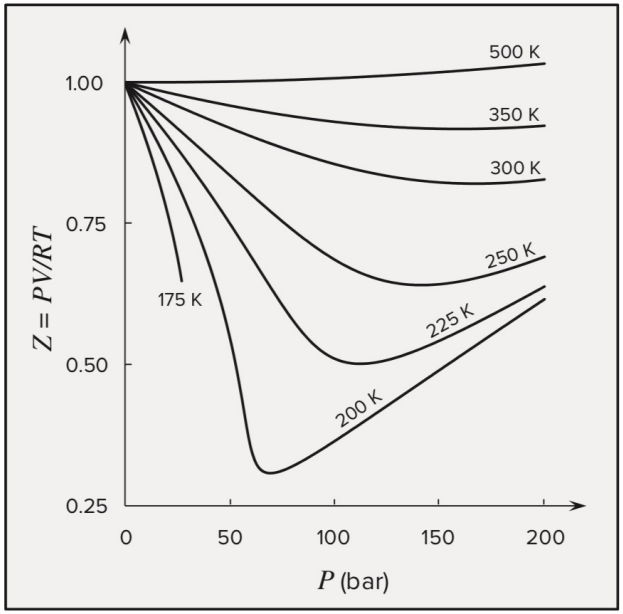
$$pV^{\gamma} = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

$$T^{\gamma}P^{1-\gamma} = \text{cosntant}$$

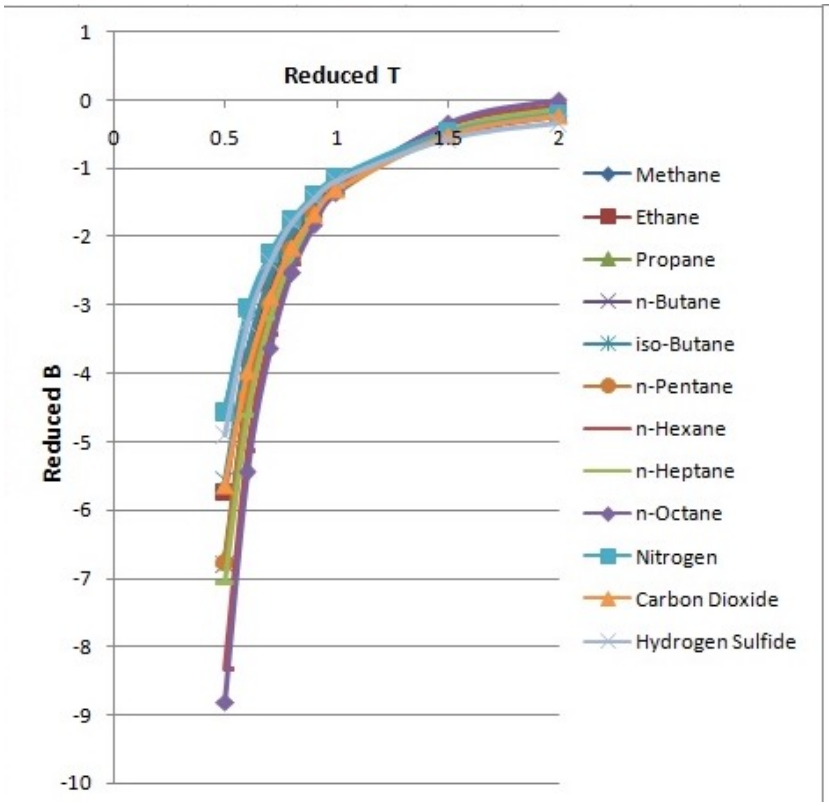
Virial EOS

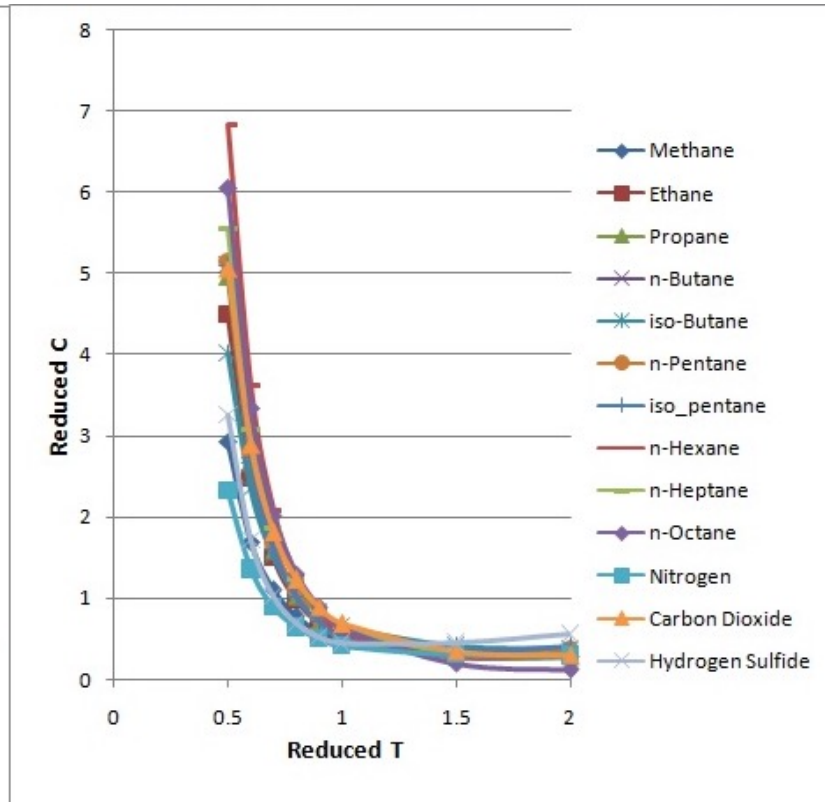
- Compressibility factor: $Z \equiv \frac{PV}{nRT}$
- Pressure expression: $Z = 1 + B'P + C'P^2 + D'P^3 + \cdots$
- Volume expression: $Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots$



Compressibility factor graph for methane

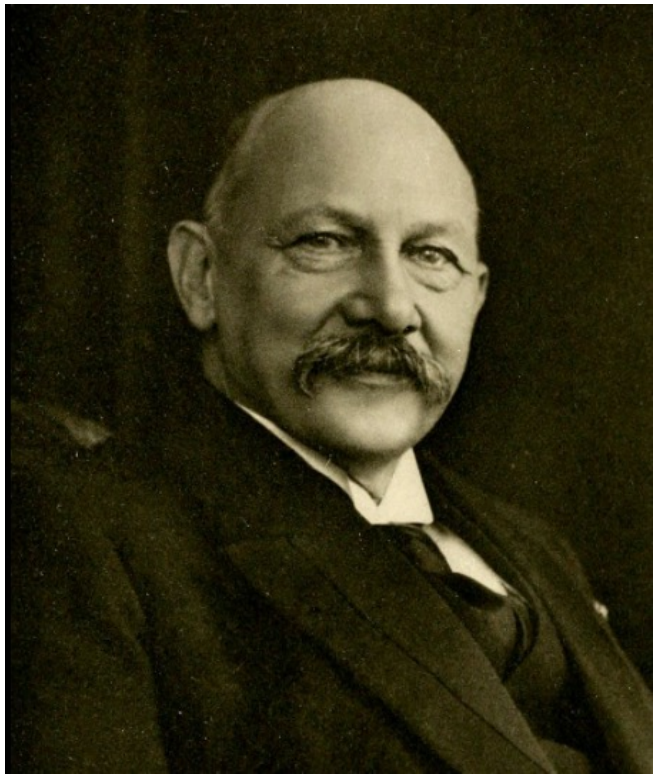
Virial EOS





Virial: vis (Latin), force, energy
by Clausius, 1870.

Virial EOS



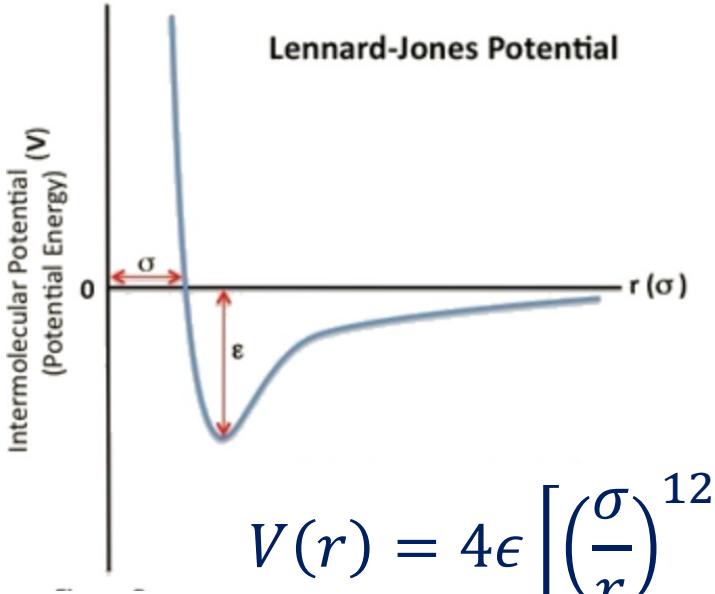
Heike K. Onnes
(1853-1926)

van der Waals EOS

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

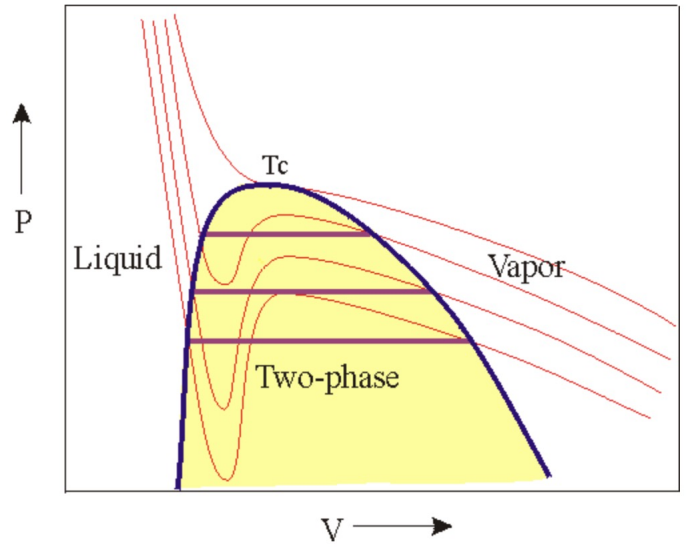
$$P = \frac{RT}{V_n - b} - \frac{a}{V_n^2}$$

- a: attractive force between molecules
- b: molecular volume



$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Isotherms



Reduced van der Waals EOS

$$p_R = \frac{8T_R}{3T_R - 1} - \frac{3}{V_R^2}$$

$$p_R = \frac{P}{P_c}, T_R = \frac{T}{T_c}, V_R = \frac{V_n}{V_{n,c}}$$

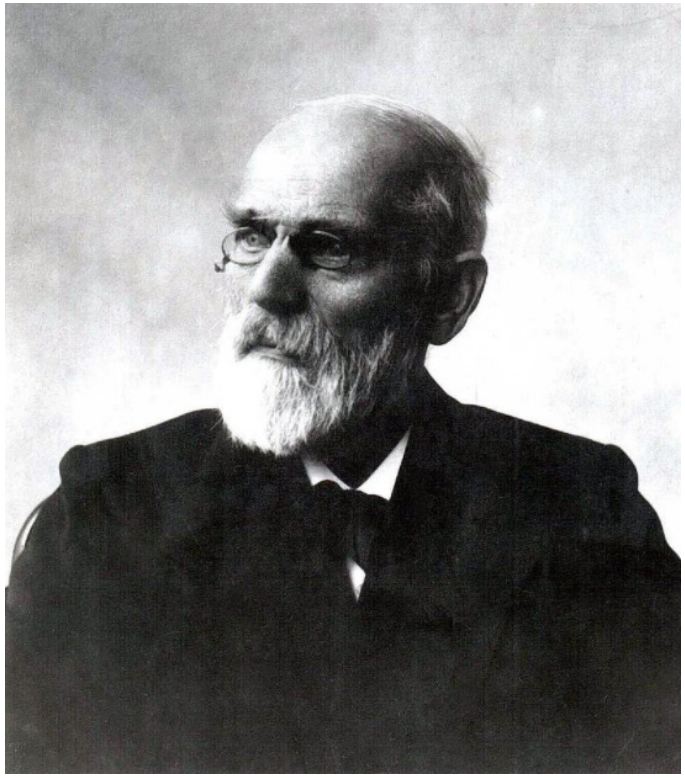
Example

Carbon dioxide

$$a = 0.3640 \ \mathrm{m}^6 \cdot \mathrm{pa} \cdot \mathrm{mol}^{-2}$$
$$b = 4.267 \times 10^{-5} \ \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$$

$$P = \frac{RT}{V_n - b} - \frac{a}{V_n^2}$$

van der Waals



Johannes van der Waals
1837-1923

Cubic EOS

- Generic cubic EOS : $P = \frac{RT}{V_n - b} - \frac{a(T)}{(V_n + \epsilon b)(V_n + \sigma b)}$
- vdW EOS (1873): $a(T) = a, \epsilon = \sigma = 0$
- RK EOS (1949): $a(T) = \frac{a}{\sqrt{T}}, \epsilon = 0, \sigma = 1$
- SRK EOS (1972): $a(T) = a\alpha(\omega), \epsilon = 0, \sigma = 1$

Peng-Robinson EOS (1976)

$$p = \frac{RT}{V_n - b} - \frac{a\alpha}{V_n^2 + 2bV_n - b^2}$$

$$a \approx 0.45724 \frac{R^2 T_c^2}{p_c}$$

$$b \approx 0.07780 \frac{RT_c}{p_c}$$

$$\alpha = \left(1 + \kappa\left(1 - T_r^{\frac{1}{2}}\right)\right)^2$$

$$\kappa \approx 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$T_r = \frac{T}{T_c}$$

Determination of EOS Parameters

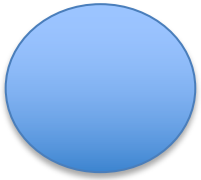
- Fitting to experimental PVT data
- Fitting to critical point

Example

- Given that the vapor pressure of n-butane at 350 K is 9.4573 bar, find the molar volumes of (a) saturated-vapor and (b) saturated-liquid n-butane at these conditions as given by the Redlich/Kwong equation.

Acentric Factor ω

- Kenneth Pitzer, 1955
- A measure of the non-sphericity of molecules
- The boiling points increase with increasing the ω
- $\omega = -\log_{10}(p_r^{sat}) - 1$ at $T_r = 0.7$
- For monatomic fluids, $\omega \approx 0$

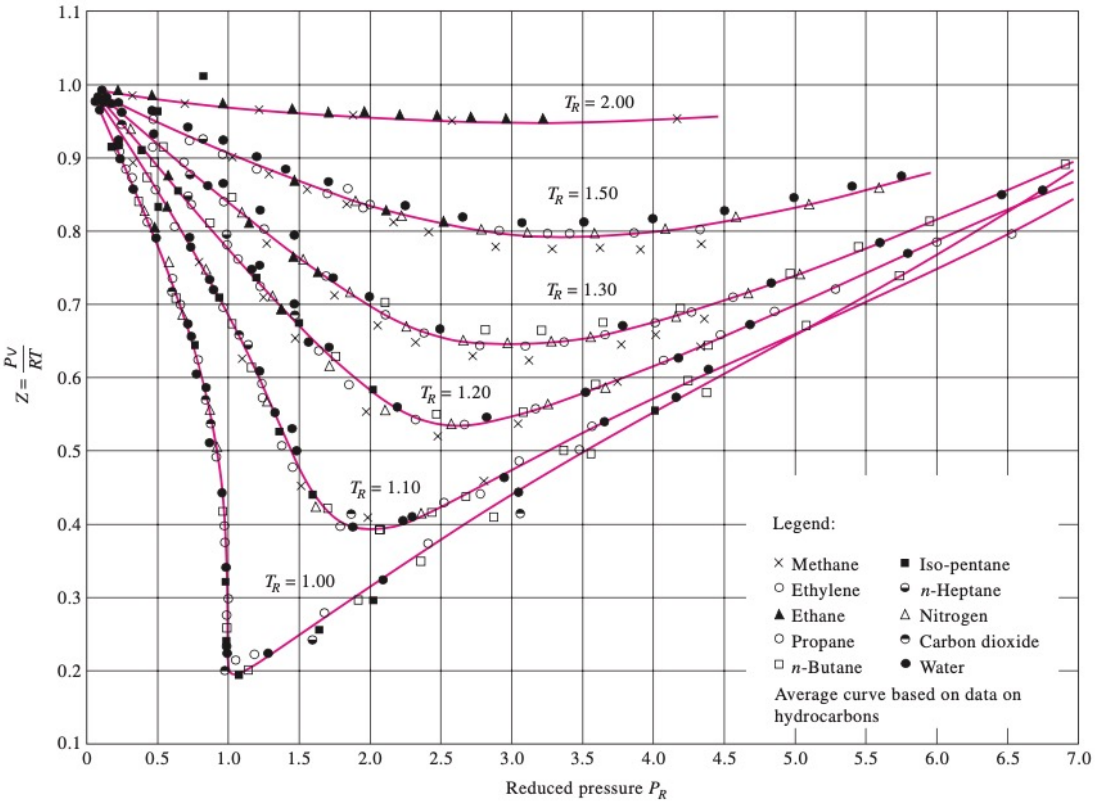


$\omega = 0$

Molecule	Acentric Factor[3]
Acetone	0.304[4]
Acetylene	0.187
Ammonia	0.253
Argon	0.000
Carbon Dioxide	0.228
Decane	0.484
Ethanol	0.644[4]
Helium	−0.390
Hydrogen	−0.220
Krypton	0.000
Methanol	0.556[4]
Neon	0.000
Nitrogen	0.040
Nitrous Oxide	0.142
Oxygen	0.022
Xenon	0.000

Two-parameters Theorem of Corresponding States

- $T_r = \frac{T}{T_c}, P_r = \frac{P}{P_c}$
- If $T_{r1} = T_{r2}, P_{r1} = P_{r2}$, then $Z_{r1} \approx Z_{r2}$
- All fluids at the same T_r, P_r have approximately the same Z_r
- Gives well prediction for simple fluids



Three-parameter Theorem of Corresponding States

- T_r, P_r, ω
- If $T_{r1} = T_{r2}, P_{r1} = P_{r2}, \omega_1 = \omega_2$, then $Z_{r1} \approx Z_{r2}$

Generalized Correlations for Gases

- $Z = Z(T_r, P_r, \omega)$
- Applicable for all gases
- Pitzer correlation

Kenneth Pitzer
(1914-1997)

Pitzer Correlations for Z

$$Z = Z^0(T_r, P_r) + \omega Z^1(T_r, P_r)$$

- $\omega = 0$: simple fluids, 2-parameters corresponding-states correlation

Table D.1: Values of Z^0

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*0.0029*	*0.0145*	*0.0290*	*0.0579*	*0.1158*	*0.1737*	*0.2315*	0.2892
0.35	*0.0026*	*0.0130*	*0.0261*	*0.0522*	*0.1043*	*0.1564*	*0.2084*	0.2604
0.40	*0.0024*	*0.0119*	*0.0239*	*0.0477*	*0.0953*	*0.1429*	*0.1904*	0.2379
0.45	*0.0022*	*0.0110*	*0.0221*	*0.0442*	*0.0882*	*0.1322*	*0.1762*	0.2200
0.50	*0.0021*	*0.0103*	*0.0207*	*0.0413*	*0.0825*	*0.1236*	*0.1647*	0.2056
0.55	0.9804	*0.0098*	*0.0195*	*0.0390*	*0.0778*	*0.1166*	*0.1553*	0.1939
0.60	0.9849	*0.0093*	*0.0186*	*0.0371*	*0.0741*	*0.1109*	*0.1476*	0.1842
0.65	0.9881	0.9377	*0.0178*	*0.0356*	*0.0710*	*0.1063*	*0.1415*	0.1765
0.70	0.9904	0.9504	0.8958	*0.0344*	*0.0687*	*0.1027*	*0.1366*	0.1703
0.75	0.9922	0.9598	0.9165	*0.0336*	*0.0670*	*0.1001*	*0.1330*	0.1656
0.80	0.9935	0.9669	0.9319	0.8539	*0.0661*	*0.0985*	*0.1307*	0.1626
0.85	0.9946	0.9725	0.9436	0.8810	*0.0661*	*0.0983*	*0.1301*	0.1614
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	*0.1006*	*0.1321*	0.1630
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	*0.1359*	0.1664
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	*0.1410*	0.1705

Table D.2: Values of Z^1

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*−0.0008*	*−0.0040*	*−0.0081*	*−0.0161*	*−0.0323*	*−0.0484*	*−0.0645*	−0.0806
0.35	*−0.0009*	*−0.0046*	*−0.0093*	*−0.0185*	*−0.0370*	*−0.0554*	*−0.0738*	−0.0921
0.40	*−0.0010*	*−0.0048*	*−0.0095*	*−0.0190*	*−0.0380*	*−0.0570*	*−0.0758*	−0.0946
0.45	*−0.0009*	*−0.0047*	*−0.0094*	*−0.0187*	*−0.0374*	*−0.0560*	*−0.0745*	−0.0929
0.50	*−0.0009*	*−0.0045*	*−0.0090*	*−0.0181*	*−0.0360*	*−0.0539*	*−0.0716*	−0.0893
0.55	−0.0314	*−0.0043*	*−0.0086*	*−0.0172*	*−0.0343*	*−0.0513*	*−0.0682*	−0.0849
0.60	−0.0205	*−0.0041*	*−0.0082*	*−0.0164*	*−0.0326*	*−0.0487*	*−0.0646*	−0.0803
0.65	−0.0137	−0.0772	*−0.0078*	*−0.0156*	*−0.0309*	*−0.0461*	*−0.0611*	−0.0759
0.70	−0.0093	−0.0507	−0.1161	*−0.0148*	*−0.0294*	*−0.0438*	*−0.0579*	−0.0718
0.75	−0.0064	−0.0339	−0.0744	*−0.0143*	*−0.0282*	*−0.0417*	*−0.0550*	−0.0681

Pitzer Correlations for *B*

$$Z = 1 + \hat{B}\frac{P_r}{T_r}$$

$$\hat{B} = \frac{BP_c}{RT_c} = B^0 + \omega B^1$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}, B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

- $Z^0 = 1 + B^0\frac{P_r}{T_r}, Z^1 = B^1\frac{P_r}{T_r}$
- Useful only where Z^0, Z^1 are approximately linear function of P_r
- Good as $T_r \geq 3$

Example

- Determine the molar volume of n-butane at 510 K and 25 bar based on each of the following:

(a) The ideal-gas state

(b) The generalized compressibility-factor correlation.

Evaluation of Z^0

Table D.1: Values of Z^0

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*0.0029*	*0.0145*	*0.0290*	*0.0579*	*0.1158*	*0.1737*	*0.2315*	0.2892
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0.40	*0.0024*	*0.0119*	*0.0239*	*0.0477*	*0.0953*	*0.1429*	*0.1904*	0.2379
0.45	*0.0022*	*0.0110*	*0.0221*	*0.0442*	*0.0882*	*0.1322*	*0.1762*	0.2200
0.50	*0.0021*	*0.0103*	*0.0207*	*0.0413*	*0.0825*	*0.1236*	*0.1647*	0.2056
0.55	0.9804	*0.0098*	*0.0195*	*0.0390*	*0.0778*	*0.1166*	*0.1553*	0.1939
0.60	0.9849	*0.0093*	*0.0186*	*0.0371*	*0.0741*	*0.1109*	*0.1476*	0.1842
0.65	0.9881	0.9377	*0.0178*	*0.0356*	*0.0710*	*0.1063*	*0.1415*	0.1765
0.70	0.9904	0.9504	0.8958	*0.0344*	*0.0687*	*0.1027*	*0.1366*	0.1703
0.75	0.9922	0.9598	0.9165	*0.0336*	*0.0670*	*0.1001*	*0.1330*	0.1656
0.80	0.9935	0.9669	0.9319	0.8539	*0.0661*	*0.0985*	*0.1307*	0.1626
0.85	0.9946	0.9725	0.9436	0.8810	*0.0661*	*0.0983*	*0.1301*	0.1614
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	*0.1006*	*0.1321*	0.1630
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	*0.1359*	0.1664
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	*0.1410*	0.1705
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6355	0.2901
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710	0.5146
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858

Evaluation of ω

Table B.1: Characteristic Properties of Pure Species

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c $cm^3 \cdot mol^{-1}$	T_n/K
Methane	16.043	0.012	190.6	45.99	0.286	98.6	111.4
Ethane	30.070	0.100	305.3	48.72	0.279	145.5	184.6
Propane	44.097	0.152	369.8	42.48	0.276	200.0	231.1
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7
n-Pentane	72.150	0.252	469.7	33.70	0.270	313.	309.2
n-Hexane	86.177	0.301	507.6	30.25	0.266	371.	341.9
n-Heptane	100.204	0.350	540.2	27.40	0.261	428.	371.6
n-Octane	114.231	0.400	568.7	24.90	0.256	486.	398.8
n-Nonane	128.258	0.444	594.6	22.90	0.252	544.	424.0
n-Decane	142.285	0.492	617.7	21.10	0.247	600.	447.3
Isobutane	58.123	0.181	408.1	36.48	0.282	262.7	261.4
Isooctane	114.231	0.302	544.0	25.68	0.266	468.	372.4

Summary Points

- The phase rule
- PVT behavior and phase diagram
- Ideal gas
- Ideal gas EOS
- van der Waals EOS
- Virial EOS
- Generalized correlations for gases