CH365 Chemical Engineering Thermodynamics

Lesson 12
Applications of the Virial Equation

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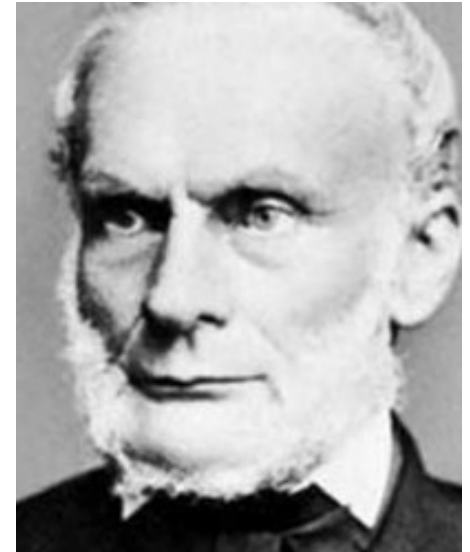
The word "virial" is derived from *vis,* the Latin word for force, strength, power, or energy, and was given its present technical definition by Rudolf Clausius in 1870. The virial theorem relates the total kinetic and potential energies of a system of particles to average of the attractive forces acting on them.

Rudolph Julius Emanuel Clausius (1822-1888) was a German physicist and mathematician and is one of the founders of modern thermodynamics. He re-stated Sadi Carnot's "Carnot Cycle" principle in terms of the 2nd Law of Thermodynamics.

The virial equation of state, the most general function relating PVT properties of fluids, was first proposed by Professor H.K. Onnes. It is a direct application of the virial theorem to chemical systems.

Clausius, RJE (1870), "On a Mechanical Theorem Applicable to Heat". Philosophical Magazine, Series 4, Vol. 40, No. 265, pp. 122–127.

Onnes, HK (1902), "Expression of State of Gases and Liquids by Means of Series," KNAW Proceedings, 4, 1901-1902, Amsterdam, pp. 125-147.

Heike Kamerlingh Onnes (1853-1926) was a Dutch physicist and Nobel laureate. He used the Hampson-Linde cycle to investigate how materials behave when cooled to nearly absolute zero and liquified helium for the first time in 1908. He is also credited with discovering superconductivity.

The "Hampson-Linde" cycle is the common vapor-liquid compression cycle used for refrigeration.
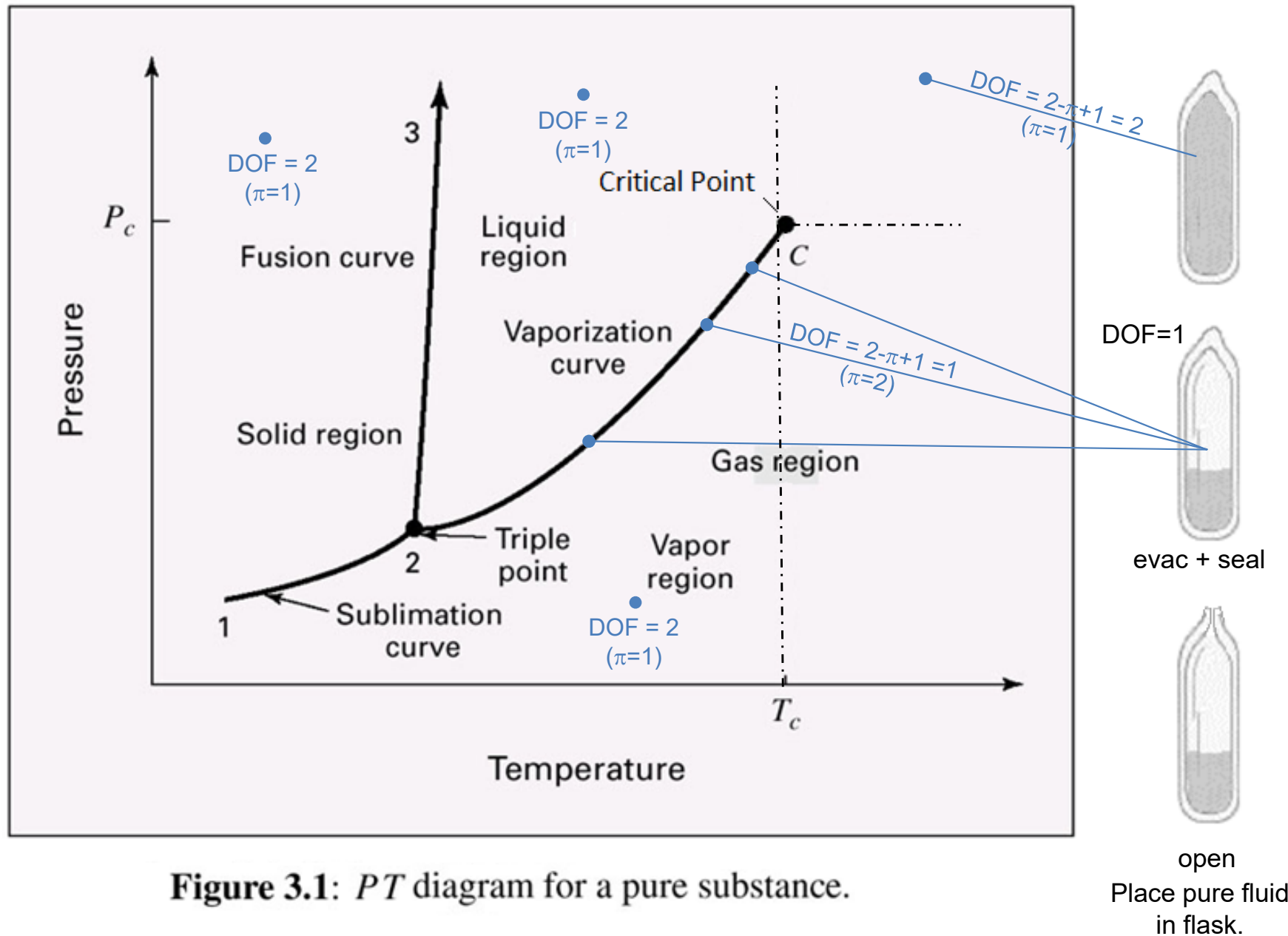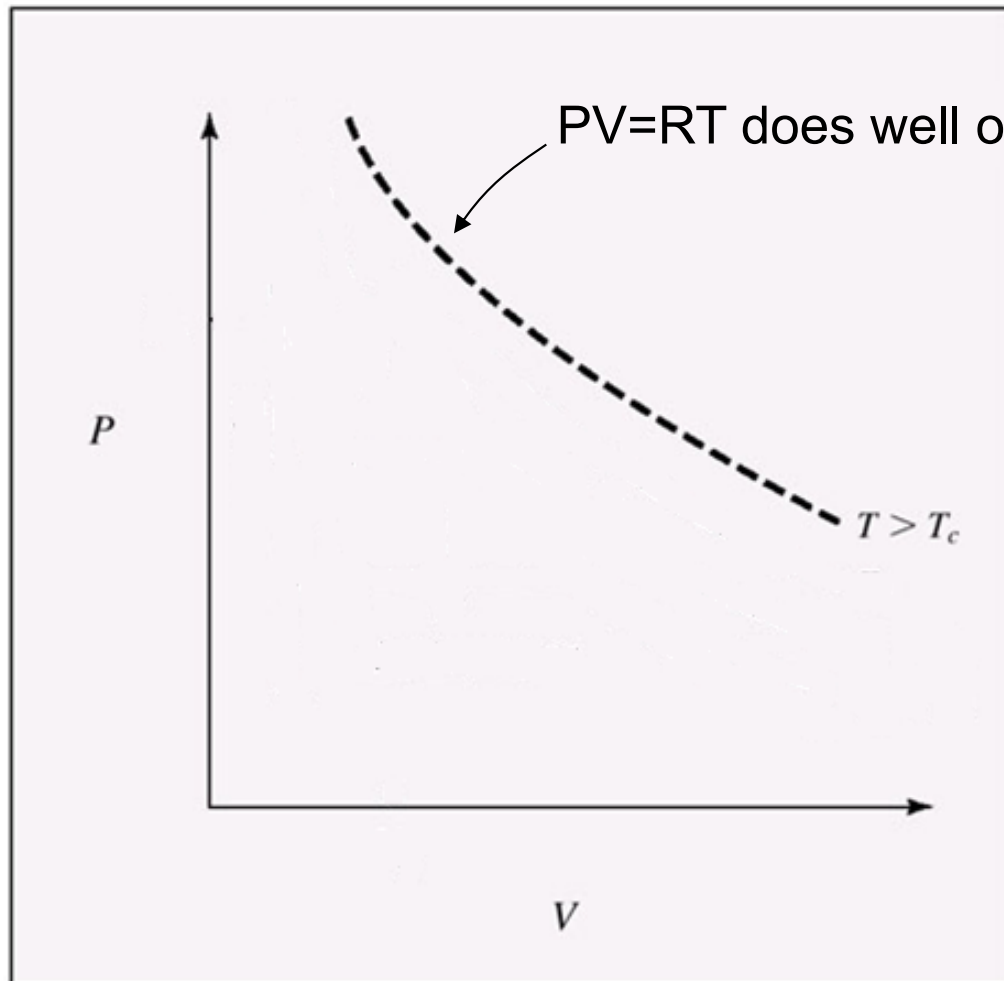
Figure 3.1: *PT* diagram for a pure substance.

Critical point – (T_c, P_c) - highest temperature and pressure at which a pure species is observed to exist in vapor/liquid equilibrium.

Vapor-Liquid Separation Processes – always operate between triple and critical points.

Ideal Gas Equation of State

$$PV = RT \implies P = \frac{const}{V}$$

PV=RT does well on this curve

P

$T > T_c$

V

Ideal gas equation of state does very well at predicting volumetric properties when $T \gg T_C$
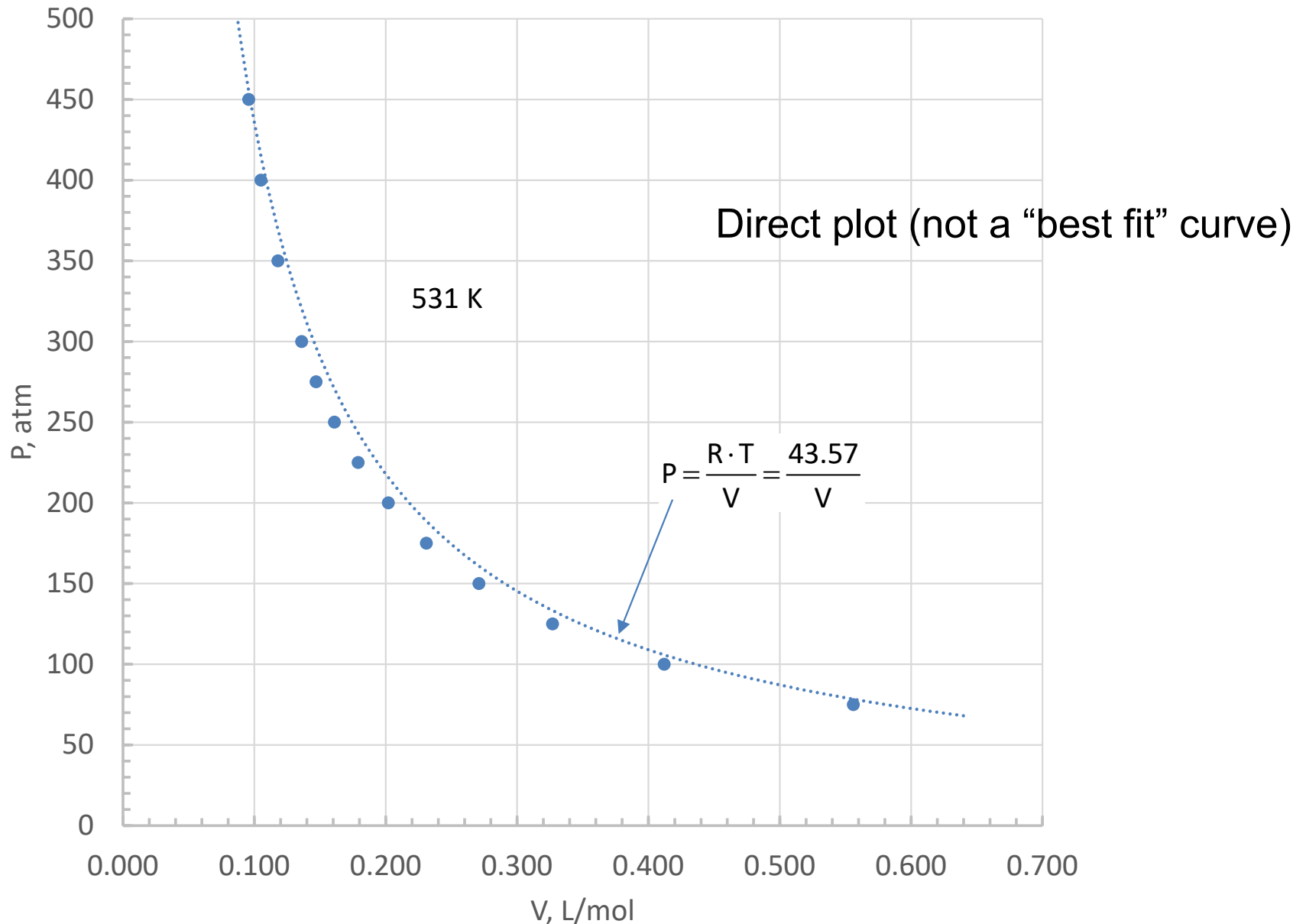
"Compressibility" form of ideal gas equation:

$$Z = \frac{PV}{RT} = 1$$

Z is defined as the compressibility factor

Problem with Ideal Gas EOS
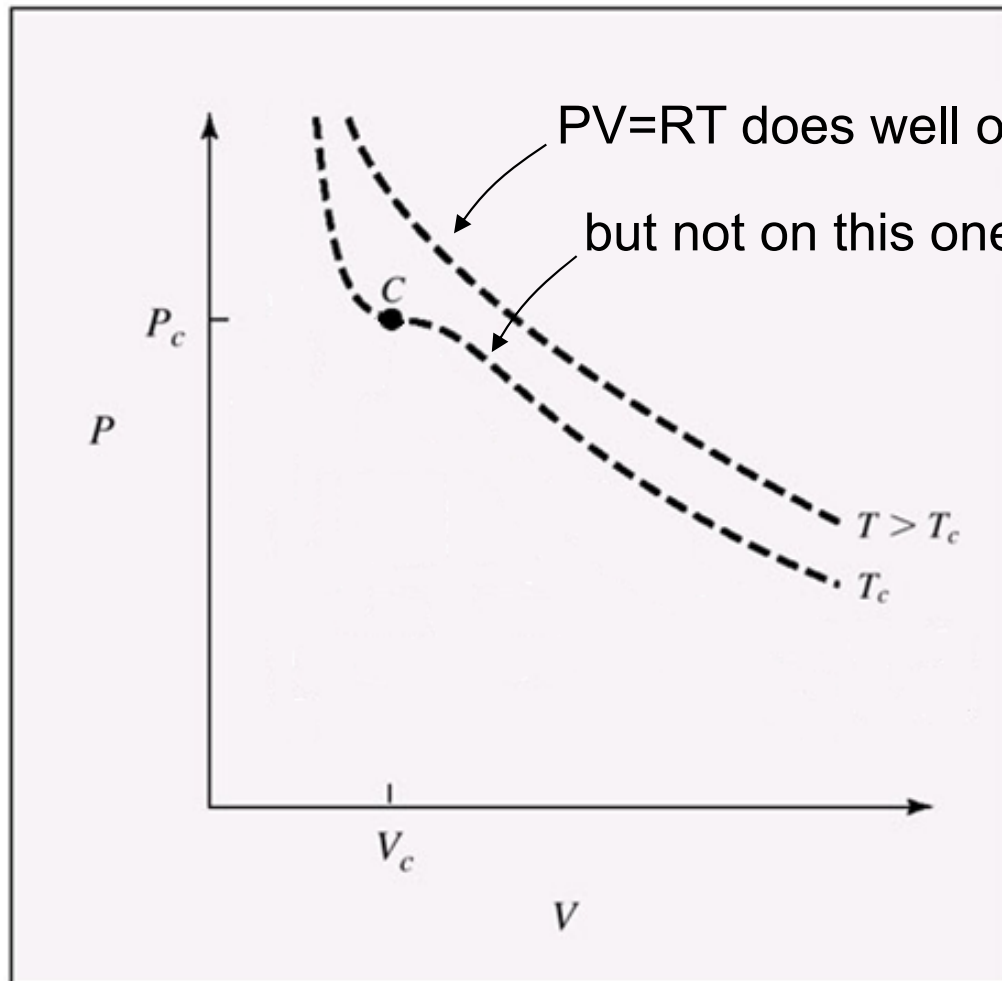
$$PV = RT \implies P = \frac{const}{V}$$

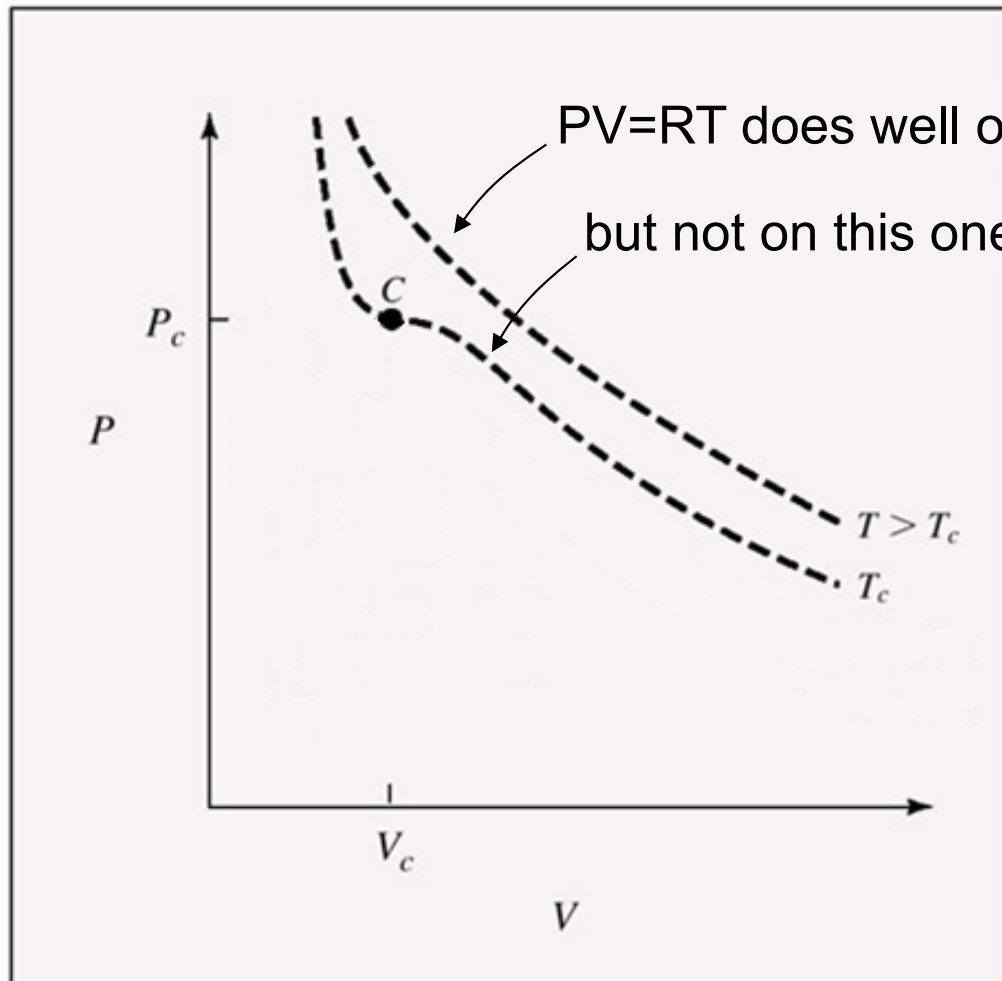PV=RT does well on this curve

but not on this one !

$$Z = \frac{PV}{RT} = \frac{V}{V_{ig}}$$

Lowering the T to near the critical temperature induces an inflection point in the curve.

Further decreases below critical temperature shows a bifurcation in the data. This situation is best handled with cubic and other more advanced EOS's.

Problem with Ideal Gas EOS

$$PV = RT \implies P = \frac{\text{const}}{V}$$

PV=RT does well on this curve

but not on this one !

P_c

P

C

$T > T_c$

T_c

V_c

V

Improved model:

$$PV = a + bP + cP^2 + dP^3 \cdots$$

$$PV = a(1 + B'P + C'P^2 + D'P^3 \cdots)$$

$$b = aB', \ c = aC', \ d = aD', \ \text{etc.}$$

"a" is found by experiment to be the same function of T for all species

Constants b, c, d, etc., are species-dependent and functions of T.
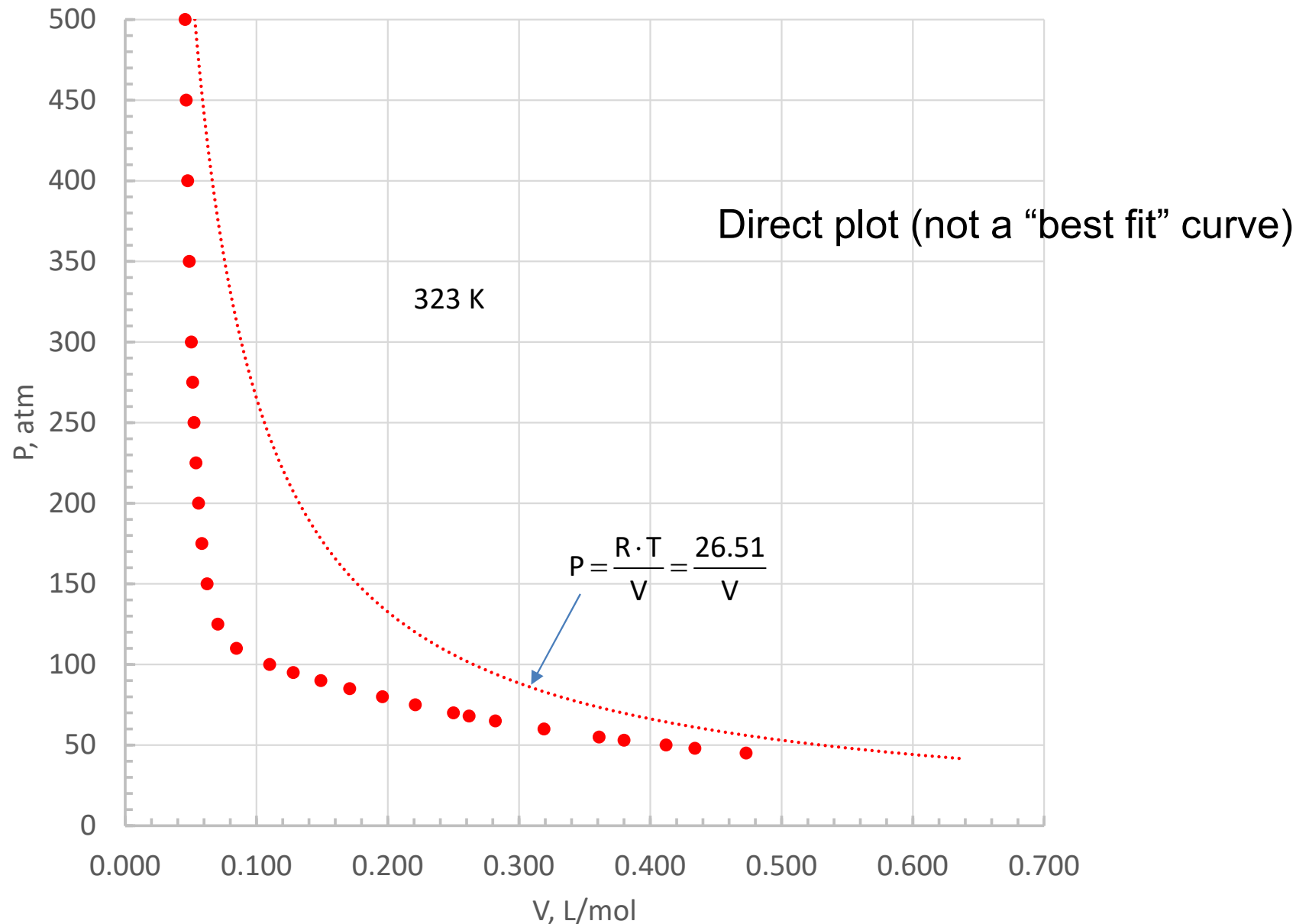
The value of b is found from high-level theory to depend on IMFs between pairs of molecules.

The constant c depends on IMFs between groups of 3 molecules (3-body IMF), d between 4, etc.
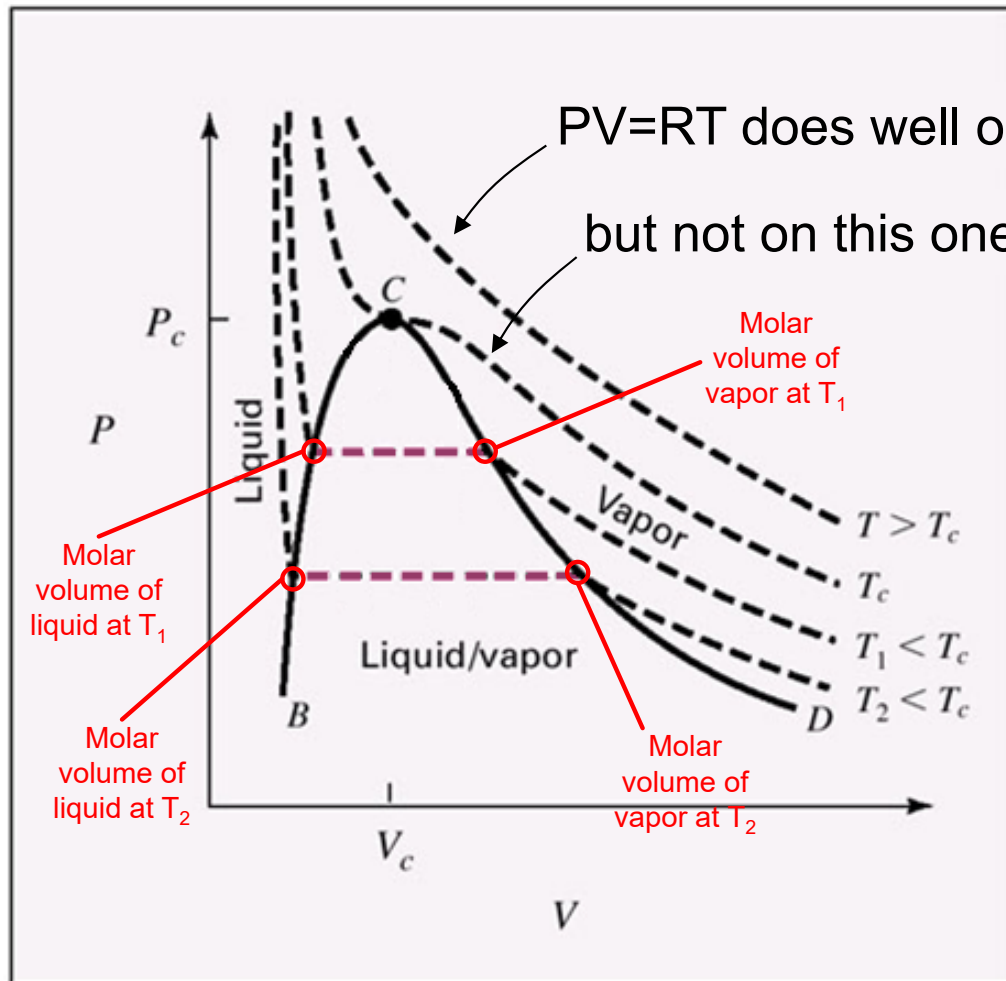
Experimental CO$_2$ Isotherms

Data from J.L. Pauley and Elwyn H. Davis, "PVT Isotherms of Real Gases,"
Journal of Chemical Education, Volume 63, Number 6, pages 466-469

Direct plot (not a "best fit" curve)

323 K

$$P = \frac{R \cdot T}{V} = \frac{26.51}{V}$$

Improved Equations of State

Virial Equation of State – First Improved Model

PV=RT does well on this curve

but not on this one !

Molar volume of vapor at T_1

Molar volume of liquid at T_1

Molar volume of liquid at T_2

Molar volume of vapor at T_2

P_c

P

Liquid

C

Vapor

$T > T_c$

T_c

$T_1 < T_c$

$T_2 < T_c$

Liquid/vapor

B

D

V_c

V

Improved model:

$$PV = a + bP + cP^2 + dP^3 \cdots$$

$$PV = a(1 + B'P + C'P^2 + D'P^3 \cdots)$$

$$b = aB', \ c = aC', \ d = aD', \ etc.$$

"a" is found by experiment to be the same function of T for all species

Constants b, c, d, etc., are species-dependent and functions of T.

The value of b is found from theory to depend on IMFs between pairs of molecules.

The constant c depends on IMFs between groups of 3 molecules (3-body IMF), d between 4, etc.

Applicability of Truncated Forms

Very useful for cases where convergence is rapid – 2 or 3 terms in the expansion
(gases and vapors at low to moderate pressures)

All isotherms
approach Z=1
as P→0

Limit of

$$\frac{PV}{RT} = \frac{a + bP + \cdots}{RT}$$

as P→0

a/RT →1

Relatively little is
known about virial
coefficients above C.

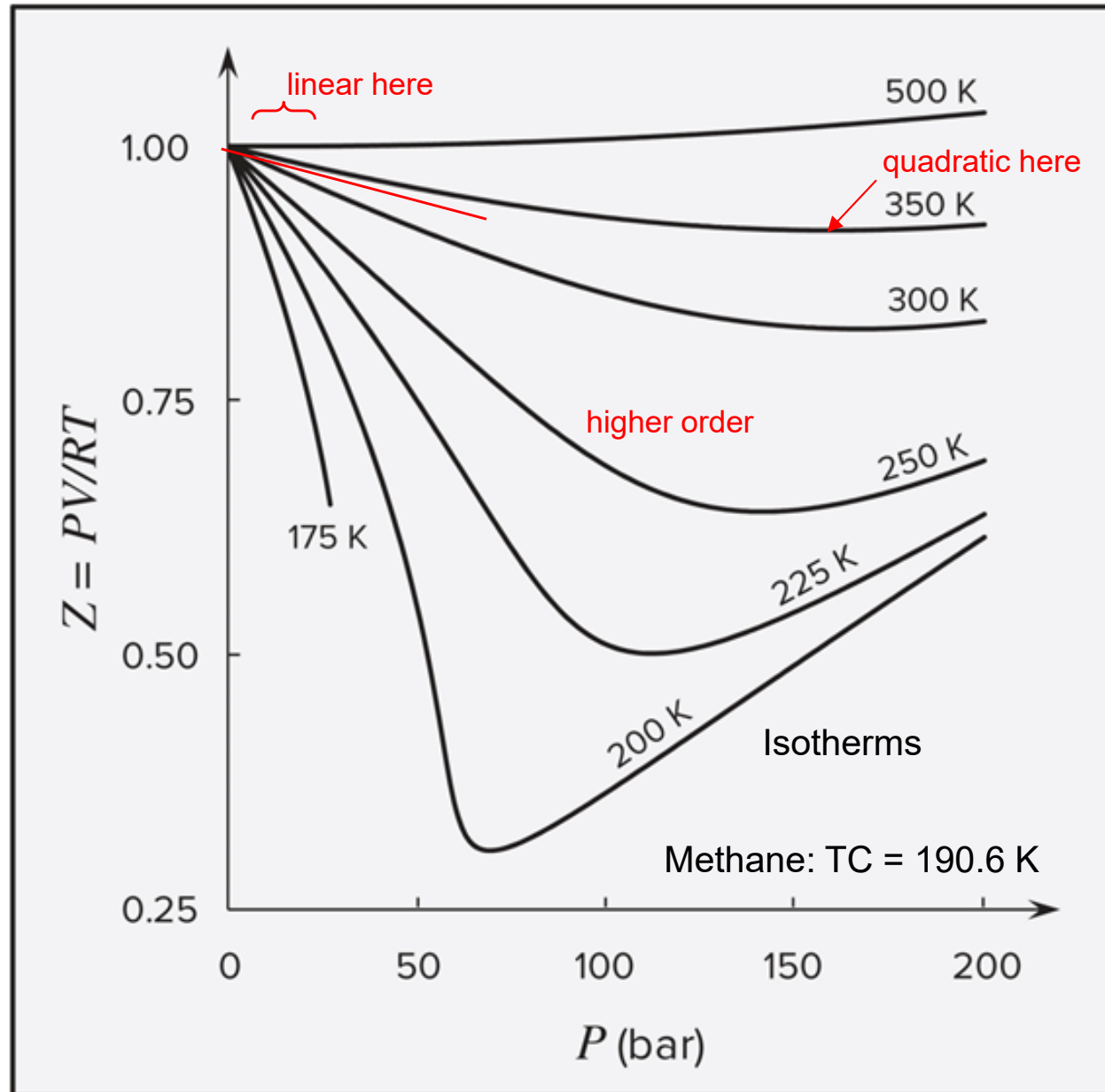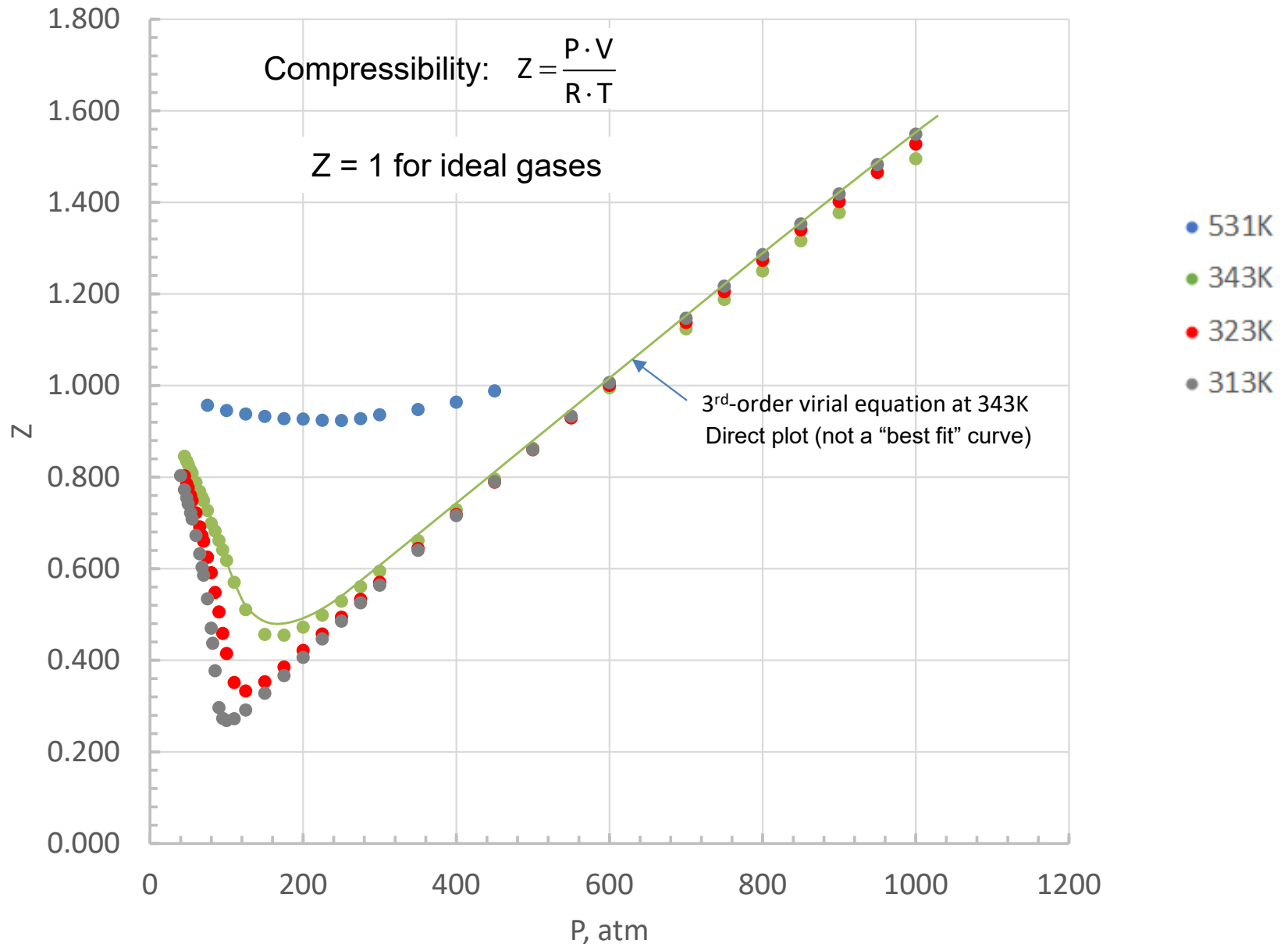Use of higher order
equations using D, E,
etc., are uncommon

Figure 3.7: Compressibility-factor graph for methane, p. 93.

Experimental CO$_2$ Isotherms

Data from J.L. Pauley and Elwyn H. Davis, "PVT Isotherms of Real Gases,"
Journal of Chemical Education, Volume 63, Number 6, pages 466-469

Compressibility: $Z = \dfrac{P \cdot V}{R \cdot T}$

Z = 1 for ideal gases

3rd-order virial equation at 343K
Direct plot (not a "best fit" curve)

- 531K
- 343K
- 323K
- 313K

Auxiliary Forms of Virial Equations

Infinite Series – Truncate to 2 or 3 terms

$$Z = 1 + B'P + C'P^2 + D'P^3 + \cdots \qquad (3.33)$$

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots \qquad (3.34)$$

Gases and vapors at low to moderate pressures

$$Z = 1 + \frac{BP}{RT} = 1 + \frac{B}{V} \qquad (3.36, 3.37)$$

2-term truncation preferred form (linear zone on slide 10)

Gases and vapors below critical point

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} \qquad (3.38)$$

3-term truncation preferred form (higher-order forms on slide 10)

(3.12 is far superior to 3.11)
(for iterative calculations)

$$B' = \frac{B}{RT}$$

(3.35a)

$$C' = \frac{C - B^2}{(RT)^2}$$

(3.35b)

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3}$$

(3.35c)

Homework

Problem 3.42

For methyl chloride at 100 degC, the second and third virial coefficients are:

$$B = -242.5 \text{ cm}^3 \text{ mol}^{-1} \quad \text{and} \quad C = 25,200 \text{ cm}^6 \text{ mol}^{-2}$$

Calculate the work of mechanically reversible, isothermal compression of 1 mole of methyl chloride from 1 bar to 55 bar at 100 degC. Base your calculations on the following forms of the virial equation:

(a) $Z = 1 + \dfrac{B}{V} + \dfrac{C}{V^2}$

(b) $Z = 1 + B'P + C'P^2$

(c) $Z = 1$

(d) $Z = 1 + \dfrac{B}{V}$

where $B' = \dfrac{B}{RT}$ and $C' = \dfrac{C - B^2}{(RT)^2}$

Suggestions for Part (a)

(ideal) $\quad P = \dfrac{RT}{V} \quad \Longleftrightarrow \quad Z = \dfrac{PV}{RT} = 1 \qquad\qquad dW = -PdV$

<div align="right">(1.3 – starting point of the textbook)</div>

(non-ideal) $\quad Z = \dfrac{PV}{RT} = 1 + \dfrac{B}{V} + \dfrac{C}{V^2}$

$$P = \left(1 + \dfrac{B}{V} + \dfrac{C}{V^2}\right)\dfrac{RT}{V}$$

substitute
for P

$$dW = -PdV = \left(1 + \dfrac{B}{V} + \dfrac{C}{V^2}\right)\dfrac{RT}{V}dV$$
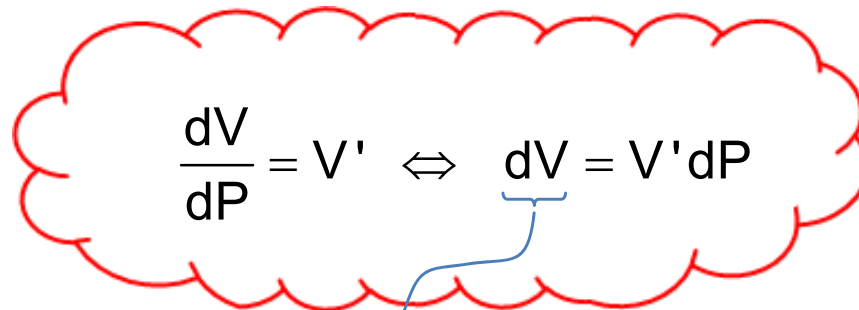
Integrate in Mathematica from V_1 to V_2.

Suggestions for Part (b)

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 \qquad\qquad dW = -PdV$$

(1.3 – starting point of the textbook)

$$V = V(P) = (1 + B'P + C'P^2)\frac{RT}{P} = \left(\frac{RT}{P} + B'P\frac{RT}{P} + C'P^2\frac{RT}{P}\right) = \left(\frac{RT}{P} + B'RT + C'RTP\right)$$

$$\frac{dV}{dP} = V' \quad\Leftrightarrow\quad dV = V'dP$$

key take-away from
lesson 10, slide 8

(constant T)

substitute for dV

$$dW = -P\,dV = -P \cdot V'dP$$

$$dV = -\frac{RT}{P^2}dP + C'RTdP = \left(C'RT - \frac{RT}{P^2}\right)dP = RT\left(C' - \frac{1}{P^2}\right)dP$$

$$dW = -PdV = -PV'dP = -P\left(RT\left(C' - \frac{1}{P^2}\right)dP\right) = -RT\left(C'P - \frac{1}{P}\right)dP$$

Integrate in Mathematica from V_1 to V_2.