Chapter 7. Properties of Real Gases

Summary

- the **ideal gas law** $pV = nRT$ is extremely useful, but reliable only at low pressures
- **equations of state for real gases** are essential for the design of engines, pipelines, and industrial equipment
- thermodynamic properties can be evaluated from equations of state to help understand real gases
- the behavior of real gases provides valuable scientific information about molecular interactions

Sections 7.1 to 7.3 Ideal and Real Gases

Ideal Gas

- no molecular interactions
- no molecular volume (point masses)

equation of state $\boxed{p = \frac{nRT}{V} = \frac{RT}{V_\mathrm{m}}}$

Real Gases

- attractive and repulsive intermolecular forces
- non-zero molecular volume
- $pV_\mathrm{m} = RT$ is a "limiting law"

$$\boxed{p = \lim_{V_\mathrm{m} \to \infty} \frac{RT}{V_\mathrm{m}}}$$

Compression Factor Z

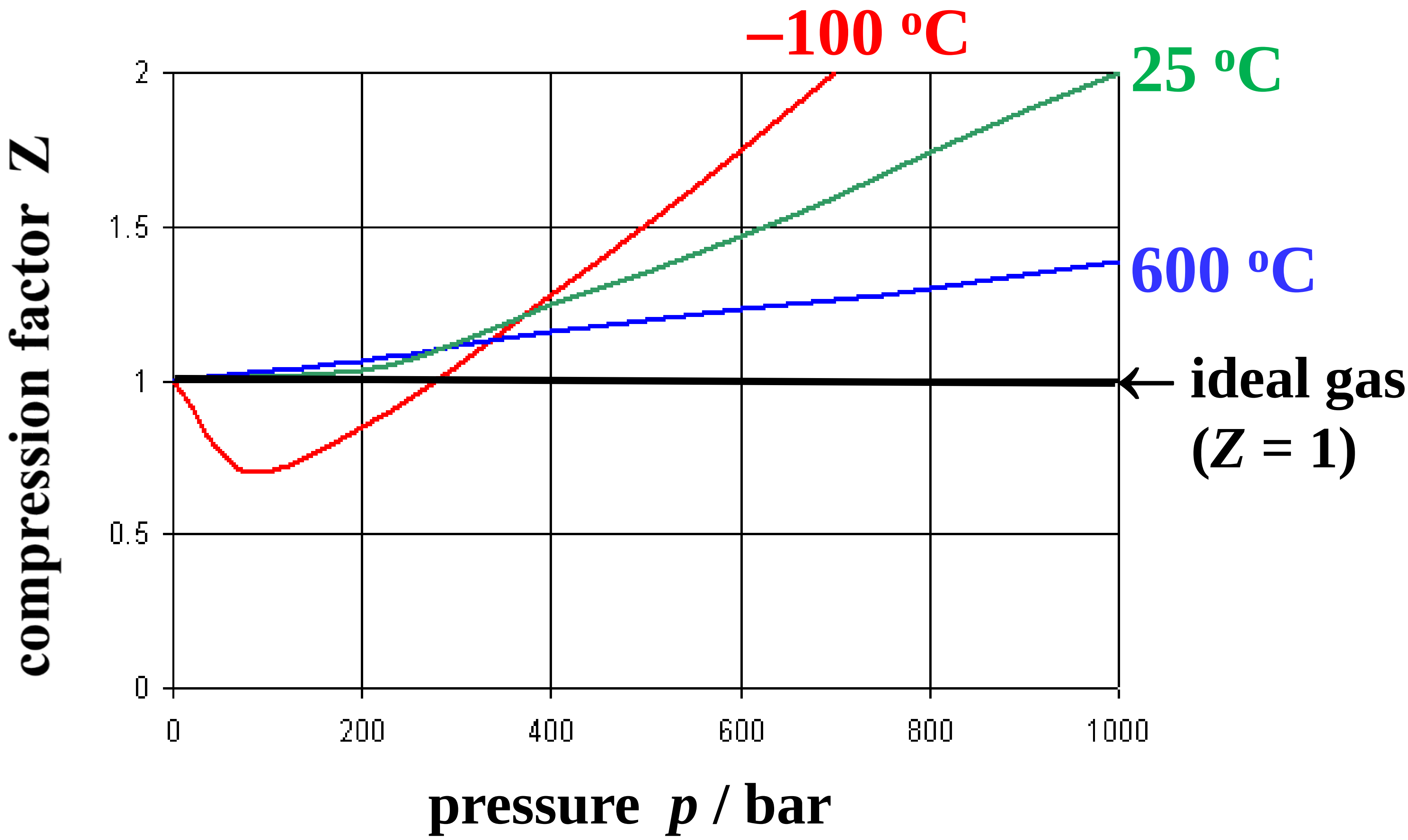
$$\boxed{Z = \frac{pV}{nRT} = \frac{pV_{\mathrm{m}}}{RT}}$$

- **Z** is dimensionless (no units)
- convenient interpretation:

$$Z = \frac{p}{\frac{nRT}{V}} = \frac{p}{p_{\mathrm{ideal}}}$$

- **$Z = 1$ for ideal gases** (at all temperatures and pressures)
- **$Z < 1$** pressure lower than expected relative to an ideal gas (attractive forces dominate, $p < p_{\mathrm{ideal}}$)
- **$Z > 1$** pressure higher than expected relative to an ideal gas (repulsive forces dominate, $p > p_{\mathrm{ideal}}$)

Compression Factor $Z = pV/nRT$ of Methane



Equations of State for Real Gases

- **van der Waals equation** $$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

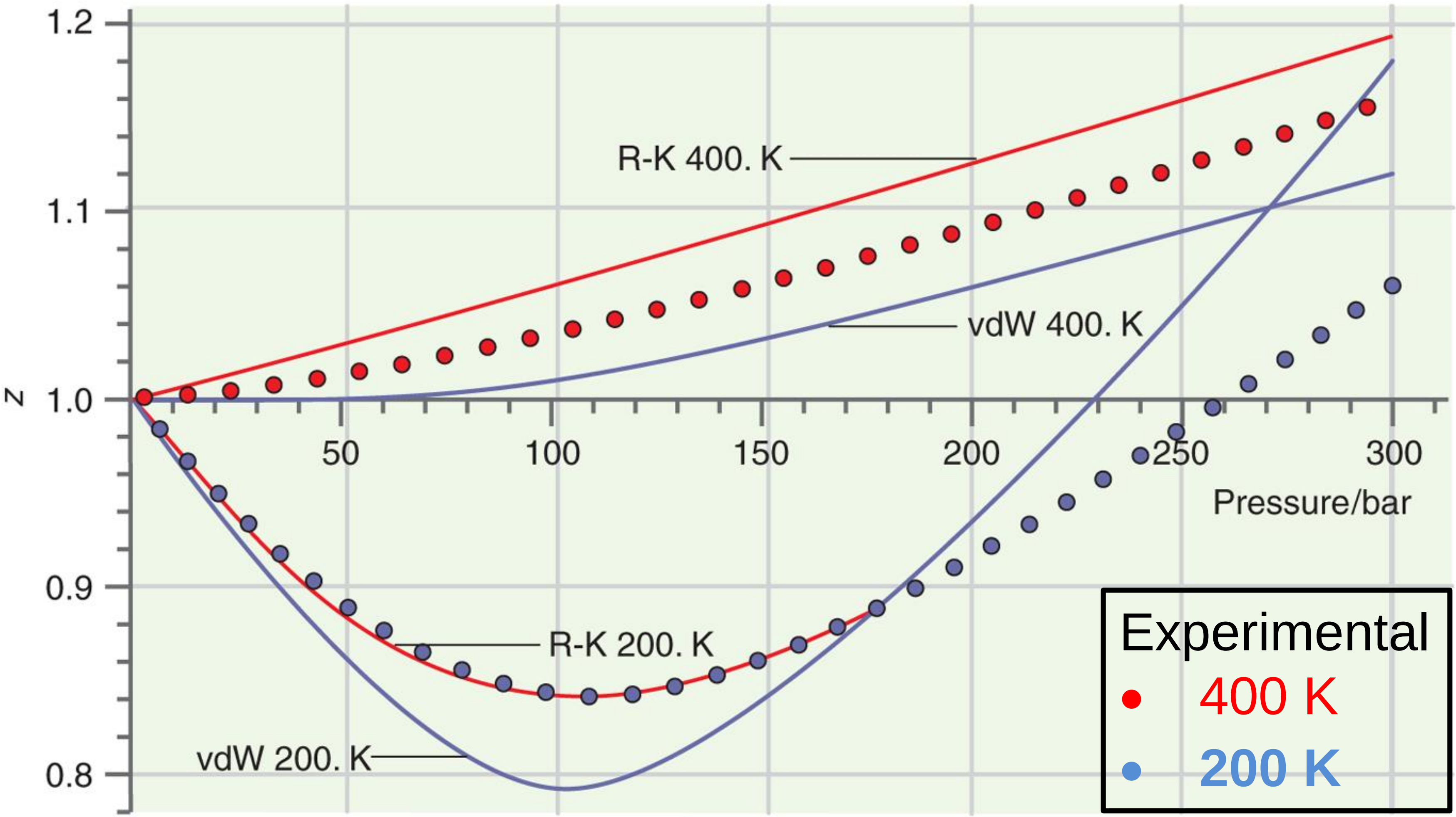
- **Redlich-Kwong equation** $$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{\sqrt{T}} \frac{1}{V_\mathrm{m}(V_\mathrm{m} + b)}$$
  (different *a* and *b* parameters)

- **virial equation** (a power series in $1/V_\mathrm{m}$)

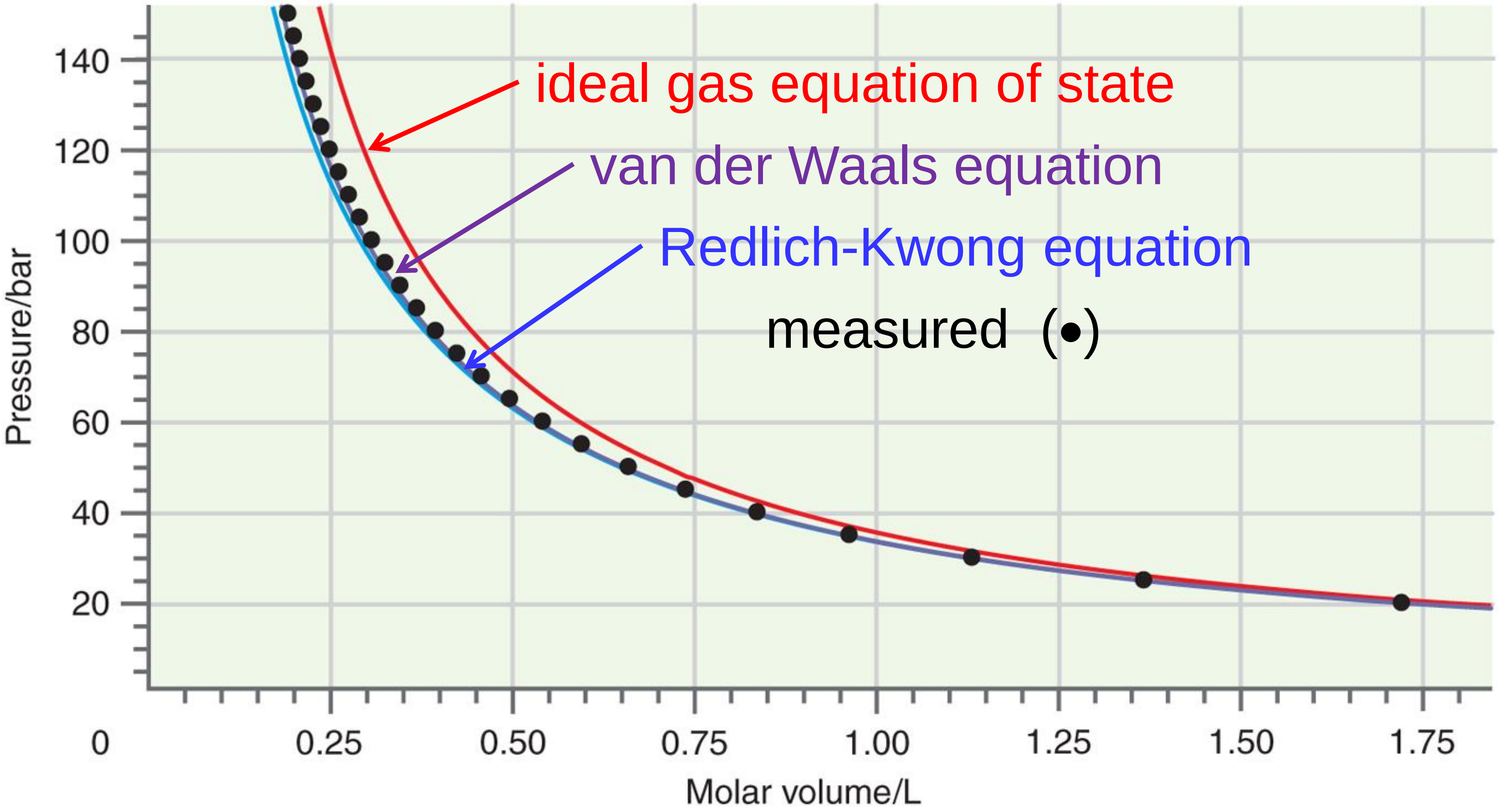
$$p = RT\left(\frac{1}{V_\mathrm{m}} + \frac{B(T)}{V_\mathrm{m}^2} + \frac{C(T)}{V_\mathrm{m}^3} + \cdots\right)$$

- **many other** equations of state are available

Compression Factor of N_2 at 200 K and 400 K



Isotherm at 426 K (153 ^{o}C) for CO_2

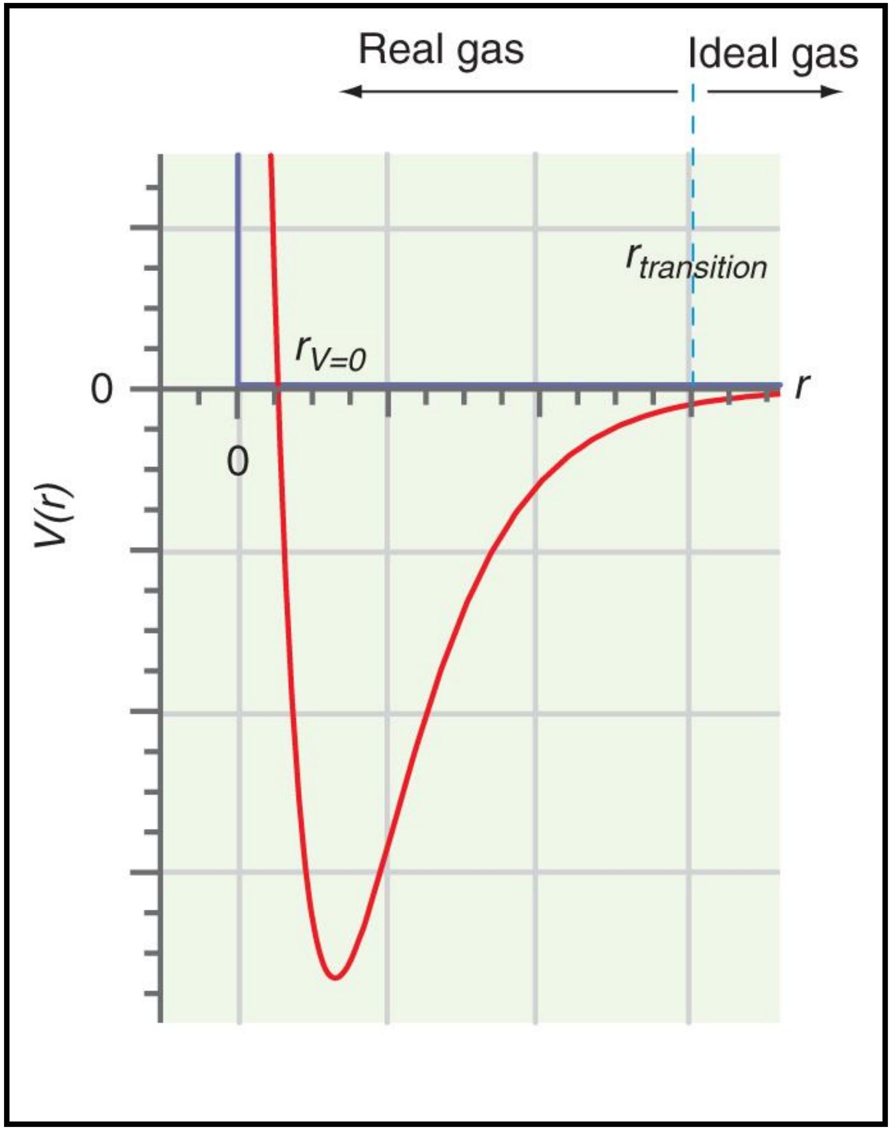


Selected van der Waals *a* and *b* Parameters

Gas	***a*** / bar L^2 mol^{-2}	***b*** / L mol^{-1}
He	0.0358	0.0240
Ne	0.220	0.0176
Ar	1.34	0.0317
Kr	2.36	0.0399
CH_4	2.28	0.0427
NH_3	4.24	0.0373
C_3H_8	9.38	0.0903

- Why does parameter ***a*** for the noble gases increase with the number of electrons per atom or molecule?
- CH_4 and NH_3 both have 10 electrons. Why is ***a*** for NH_3 significantly larger than ***a*** for CH_4?
- Parameter ***b*** is similar the molar volume of the liquefied gases.

Molecular Interactions Cause Nonideal Gas Behavior



Potential Energy *V*(*r*) of a Pair of Molecules

r = separation distance

Second Virial Coefficient

$$\boxed{B(T) = 2\pi N_A \int_0^{\infty} (1 - e^{-V(r)/kT}) r^2 \mathrm{d}r}$$

Second Virial Coefficient *B*(*T*) of an Ideal Gas that Dimerizes

$$\mathbf{A_1(g) + A_1(g) \leftrightarrow A_2(g)}$$

equilibrium constant $$K(T) = \frac{p_{\mathrm{A2}}}{p_{\mathrm{A1}}^2}$$

For small extents of dimerization, the 2nd virial coefficient is

$$\boxed{B(T) = -RTK(T)}$$

Significance This result illustrates that *B*(*T*) measures pair-wise molecular interactions.

Why is *B*(*T*) negative? One less mole of gas for every mole of A_2 dimers that forms **($\Delta n_g = -1$ mol)**.

van der Waals *a*, *b* Parameters and the 2nd Virial Coefficient *B*(*T*)

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

multiply by $\dfrac{V_\mathrm{m}}{RT}$

$$\frac{pV_\mathrm{m}}{RT} = Z = \frac{V_\mathrm{m}}{V_\mathrm{m} - b} - \frac{a}{RT}\frac{1}{V_\mathrm{m}}$$

$$= 1 + \frac{b}{V_\mathrm{m}} + \frac{b^2}{V_\mathrm{m}^2} + \frac{b^3}{V_\mathrm{m}^3} + \cdots - \frac{a}{RT}\frac{1}{V_\mathrm{m}}$$

$$= 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_\mathrm{m}} + \frac{b^2}{V_\mathrm{m}^2} + \frac{b^3}{V_\mathrm{m}^3} + \cdots$$

$$= 1 + \frac{B(T)}{V_\mathrm{m}} + \frac{C(T)}{V_\mathrm{m}^2} + \cdots$$

$$\boxed{B(T) = b - \frac{a}{RT}}$$

The second virial coefficient $B(T)$, a measure of the pairwise interaction of molecules, and the van der Waals a and b parameters are related.

$$\boxed{B(T) = b - \frac{a}{RT}}$$

Low Temperature Limit (1/$T \to \infty$)

$$B(T) = -\frac{a}{RT}$$

attractive forces dominate

High Temperature Limit (1/$T \to 0$)

$$B(T) = b$$

repulsive forces dominate

At the Boyle Temperature ($T_B = a/Rb$)

$$B(T_B) = 0 = b - \frac{a}{RT_B}$$

attractive and repulsive forces balanced

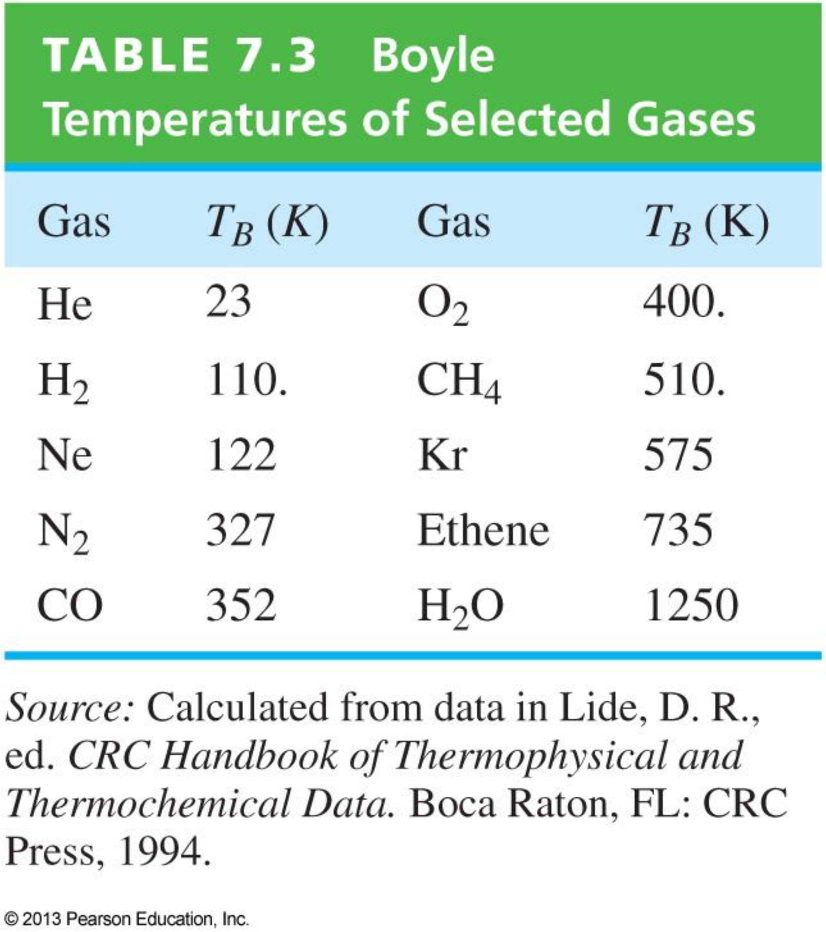


TABLE 7.3 Boyle Temperatures of Selected Gases

Gas	T_B (K)	Gas	T_B (K)
He	23	O_2	400.
H_2	110.	CH_4	510.
Ne	122	Kr	575
N_2	327	Ethene	735
CO	352	H_2O	1250

Source: Calculated from data in Lide, D. R., ed. *CRC Handbook of Thermophysical and Thermochemical Data.* Boca Raton, FL: CRC Press, 1994.

Gases can be cooled by expansion at temperatures below T_{Boyle}.

Evaluation of Second Virial Coefficient $B(T)$ from Experimental p-V-T Data

Virial equation
$$\frac{pV_\mathrm{m}}{RT} = Z = 1 + \frac{B(T)}{V_\mathrm{m}} + \frac{C(T)}{V_\mathrm{m}^2} + \cdots$$

rearranges to
$$(Z-1)V_\mathrm{m} = B(T) + \frac{C(T)}{V_\mathrm{m}} + \cdots$$

Plot $(Z-1)V_\mathrm{m}$ against $1/V_\mathrm{m}$

If the plot is linear:

intercept = $B(T)$

slope = $C(T)$

$D(T)$ and higher virial coefficients are negligible

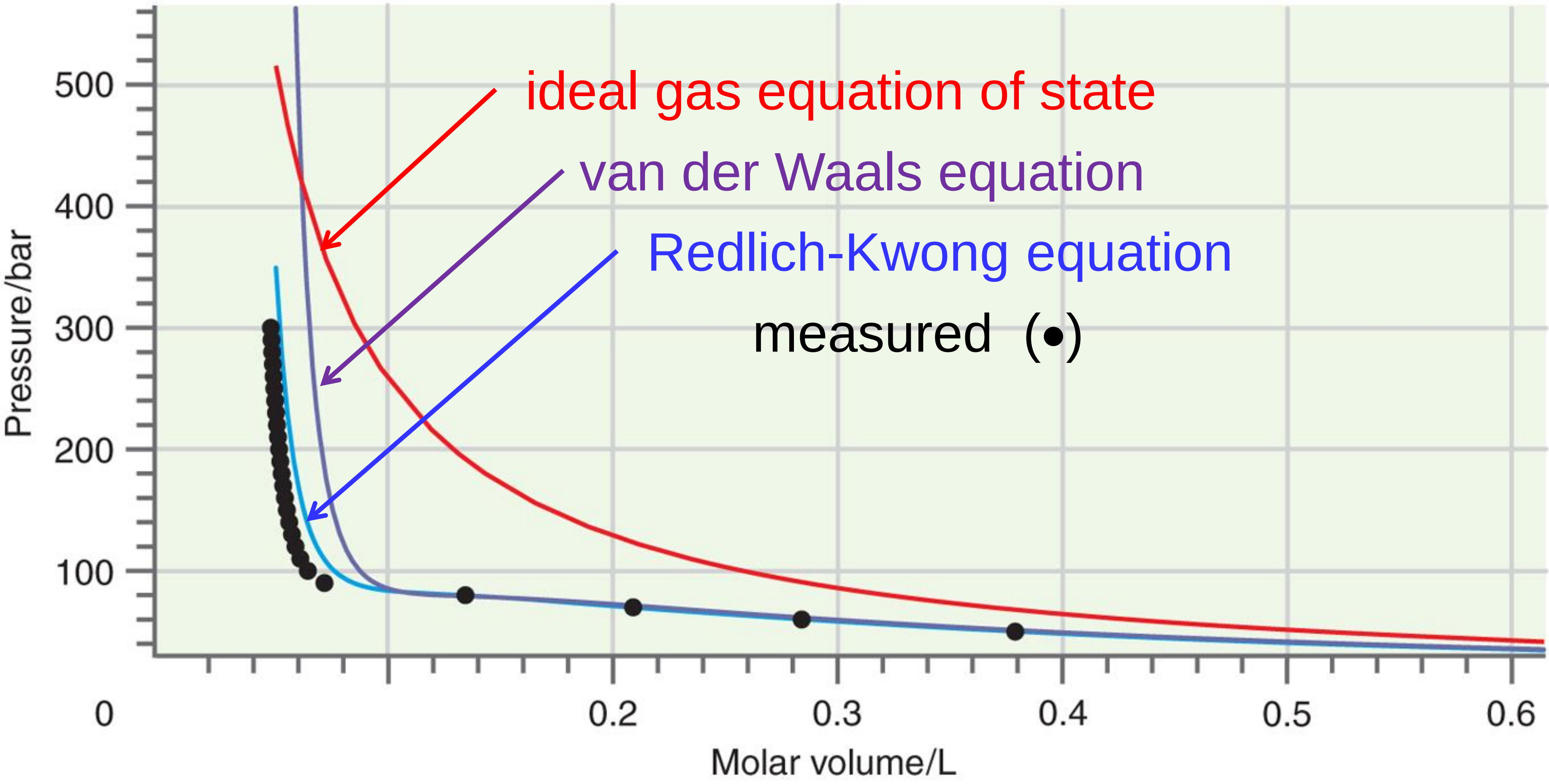
Equations of State for Gases

- ideal gas equation
- van der Waals equation
- Redlich-Kwong equation
- virial equation
- *etc.* …

!!! Warning !!!

all these equations
fail to predict gas liquefaction

Isotherm at 310 K (37 °C) for CO_2

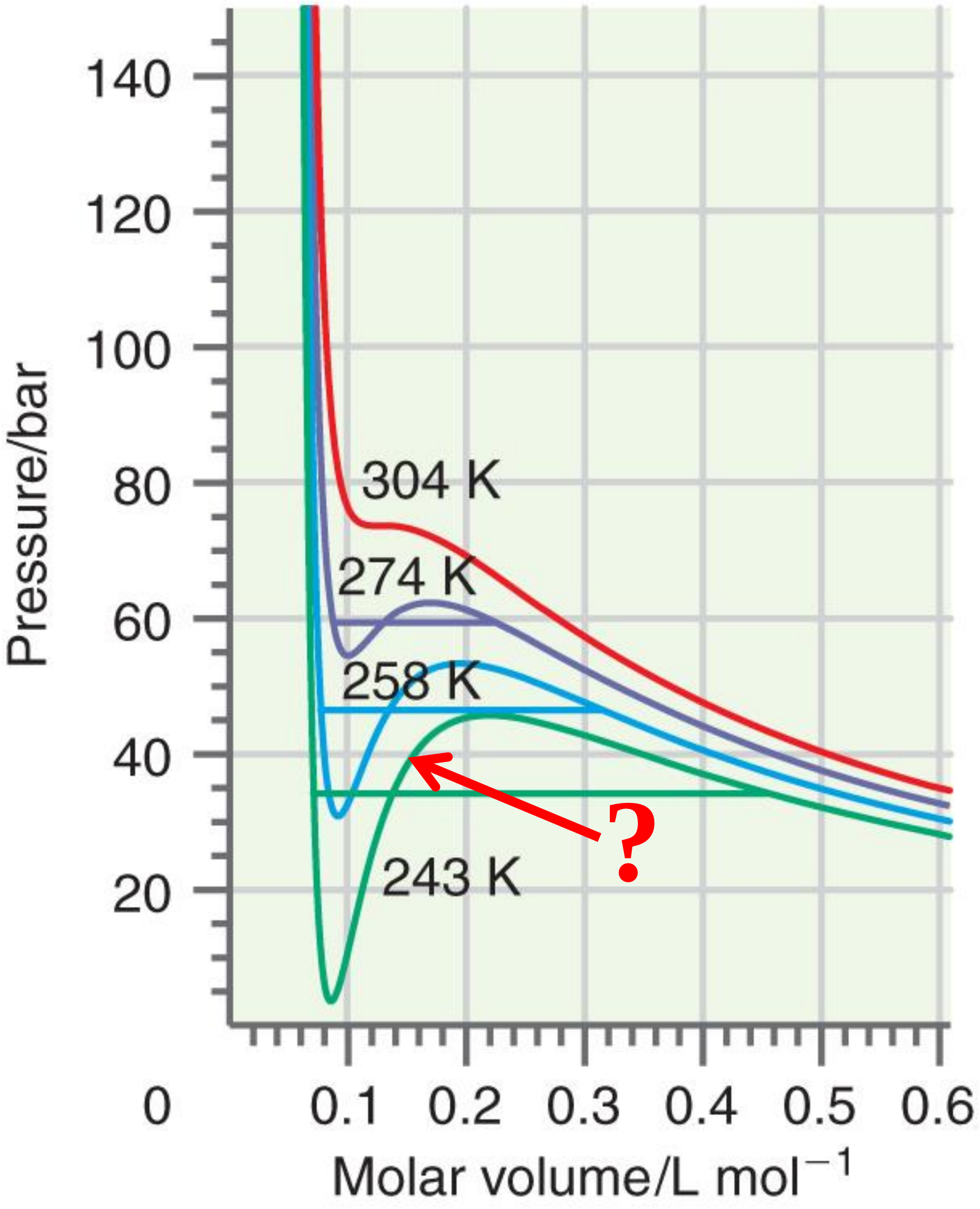


ideal gas equation of state

van der Waals equation

Redlich-Kwong equation

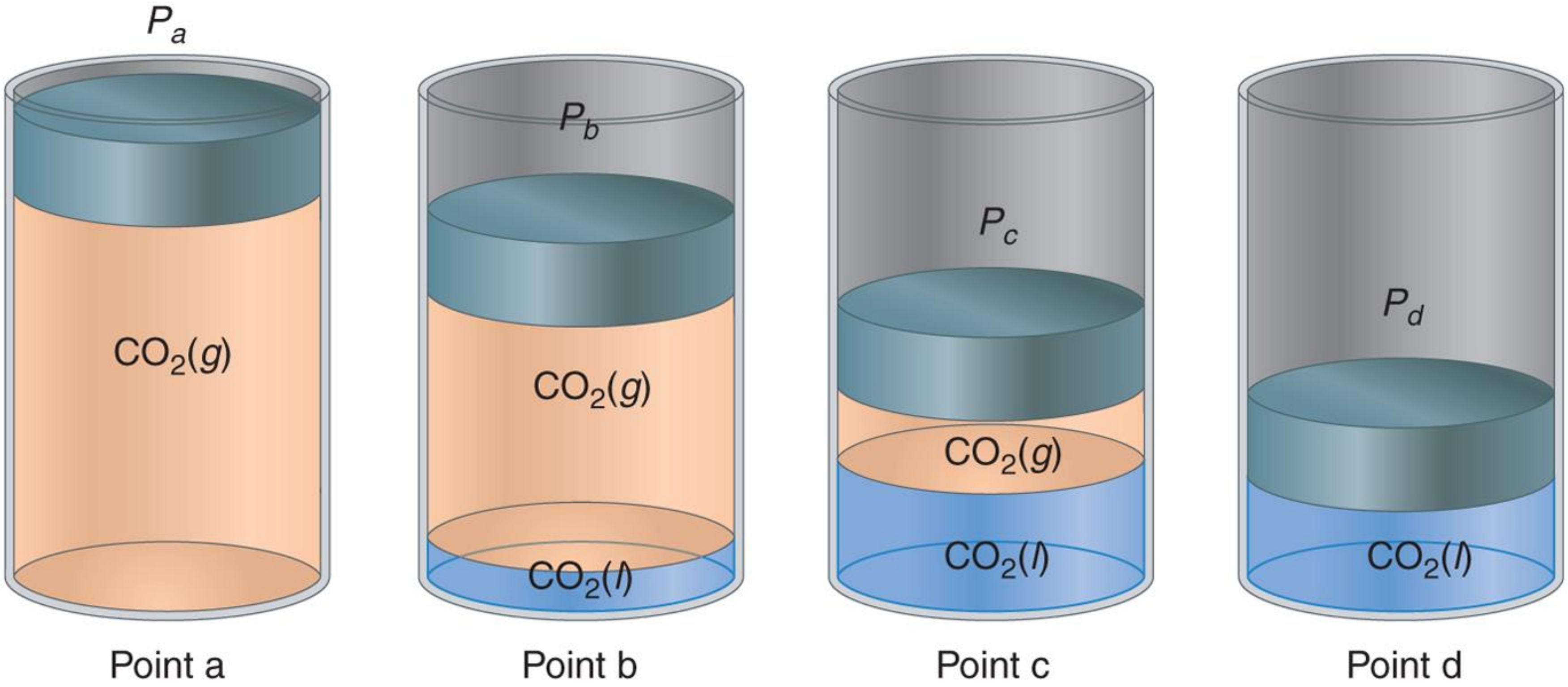
measured (●)



Van der Waals Isotherms for CO_2 in the gas + liquid region

(< 304 K)

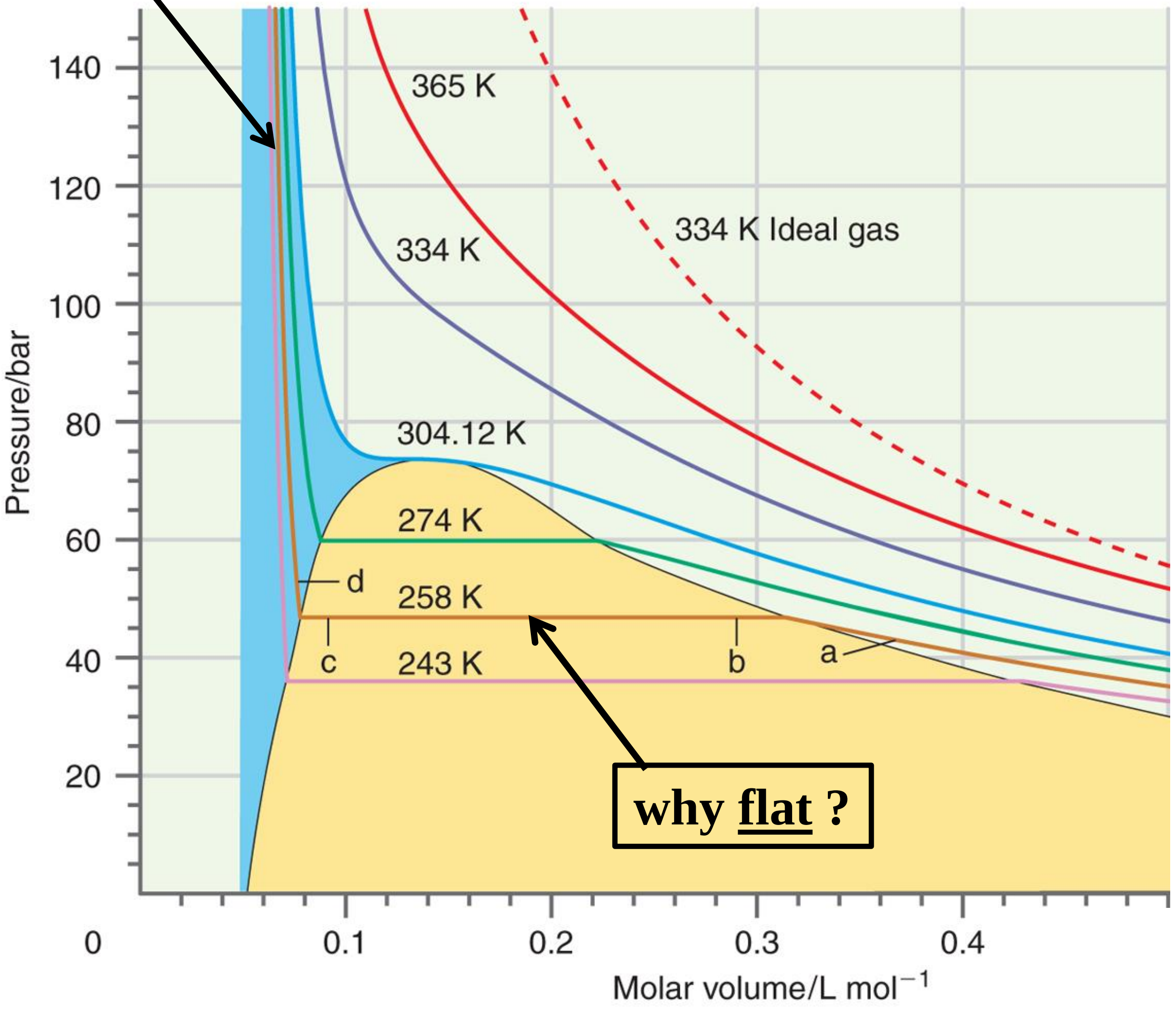
Why are the isotherms
at 274 K, 258 K, 243 K
<u>physically unreasonable</u>?


P_a
$CO_2(g)$
Point a
P_b
$CO_2(g)$
$CO_2(l)$
Point b
P_c
$CO_2(g)$
$CO_2(l)$
Point c
P_d
$CO_2(l)$
Point d

Isotherms for CO_2

Liquid CO_2 can form at temperatures below 304.12 K (30.98 ^{o}C)

why so steep ?



why flat ?

258 K isotherm

a all gas

b gas + liquid (mostly gas)

c gas + liquid (mostly liquid)

d all liquid

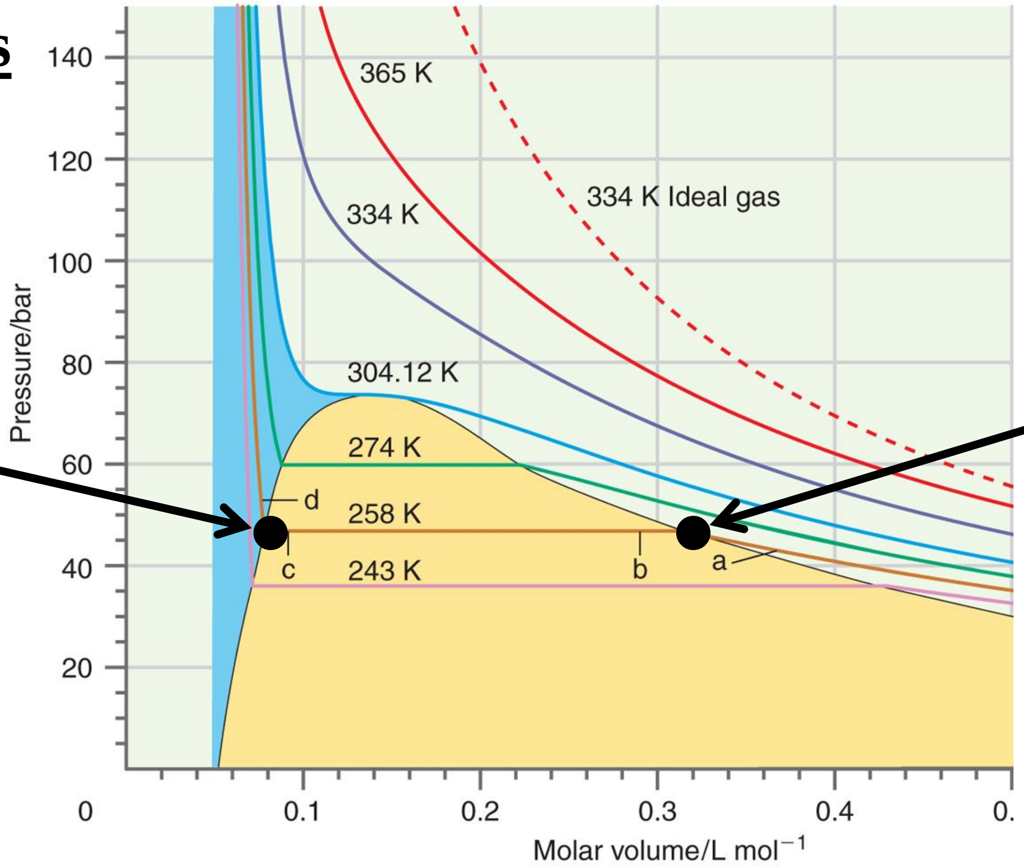
How could you tell $CO_2(g)$ and $CO_2(l)$ are in a vessel?

258 K Isotherm for CO_2

Bubble Points and Dew Points

De-compress
liquid CO_2
at 258 K.

First gas
bubbles
form here

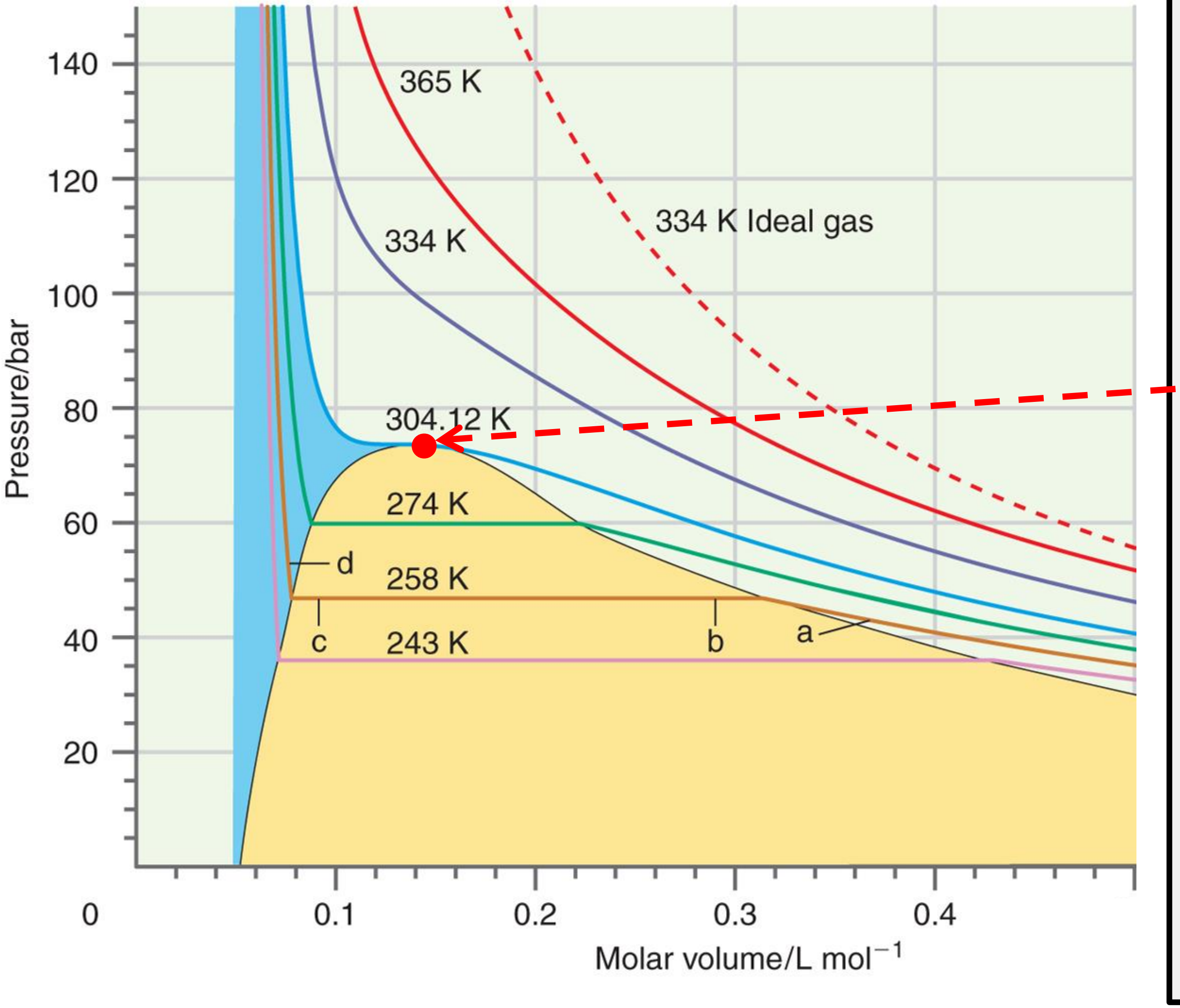


Compress
CO_2 gas
at 258 K.

First liquid
droplets
(CO_2 “dew”)
form here

Critical CO_2 **Isotherm at 304.12 K** ——

a "special" isotherm



Critical Point (●)

a mathematical inflection point

$$\left(\frac{\partial p}{\partial V_\mathrm{m}}\right)_{T=T_\mathrm{c}} = 0$$

$$\left(\frac{\partial^2 p}{\partial V_\mathrm{m}^2}\right)_{T=T_\mathrm{c}} = 0$$

at

T_c = 304.12 K

p_c = 73.75 bar

Significance of the Critical Point

$$\boxed{\left(\frac{\partial p}{\partial V_\mathrm{m}}\right)_{T=T_\mathrm{c}} = 0} \qquad \boxed{\left(\frac{\partial^2 p}{\partial V_\mathrm{m}{}^2}\right)_{T=T_\mathrm{c}} = 0}$$

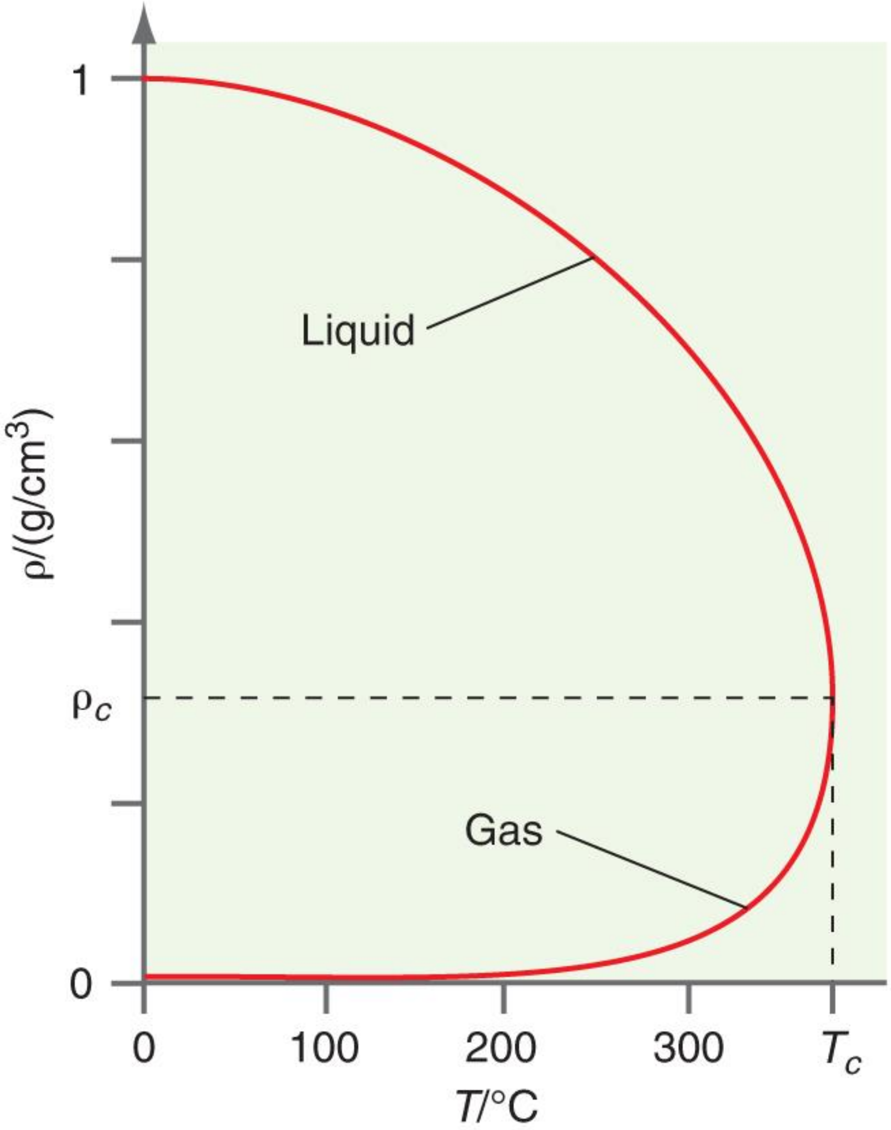
- T_c is maximum temperature at which vapor and liquid co-exist

- **approaching the critical point from lower temperatures:**
  - ♦ liquid and gas densities become identical
  - ♦ meniscus disappears
  - ♦ liquid and vapor phases form a single fluid

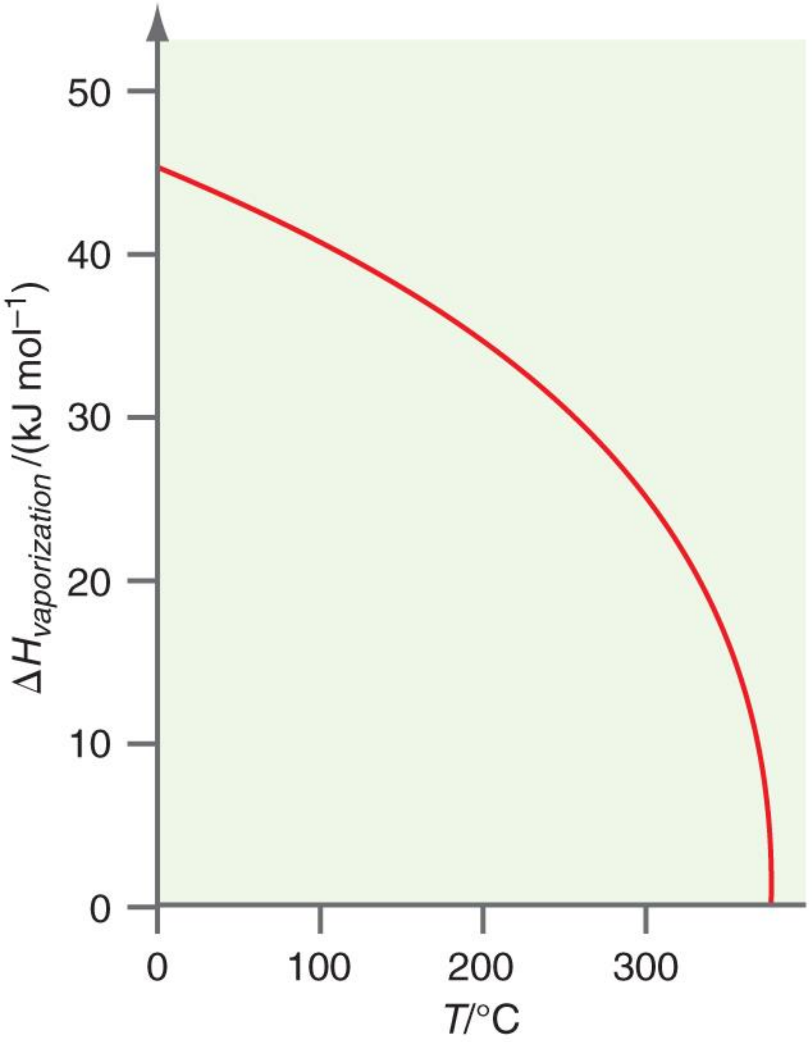
- <u>infinite isothermal compressibility</u> at the critical point

$$\kappa_T = -\frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial p}\right)_T \to \infty$$

The Densities of Liquid Water and Water Vapor Become Identical at the Critical Point



The Enthalpy of Vaporization of Water Drops to Zero at the Critical Point



Critical Constants of Pure Substances

Substance	T_c / K	p_c / bar	V_{mc} / L mol^{-1}	Z_c
He	5.25	2.27	0.0573	0.301
Ne	44.49	26.79	0.0419	0.303
Ar	150.86	48.98	0.0746	0.291
Kr	209.35	54.3	0.0923	0.288
Xe	289.74	58.4	0.1180	0.286
H_2	32.98	12.93	0.0642	0.303
O_2	154.58	50.43	0.0734	0.288
N_2	126.20	33.98	0.0901	0.292
CO_2	304.13	73.75	0.0941	0.274
CH_4	190.56	45.99	0.0986	0.286
CH_3CH_3	305.32	48.72	0.1455	0.279
$CH_3CH_2CH_3$	369.83	42.48	0.2000	0.276
H_2O	**647.14**	220.64	0.0559	**0.229**
NH_3	405.40	113.53	0.0725	**0.244**

why increasing?

why so high?

why a bit low?

Notice: T_c, p_c, and V_{mc} vary widely, but **Z_c is nearly constant** (important later).

Section 7.4 Law of Corresponding States

Instead of trying to develop van der Waals, Redlich-Kwong, virial, Beattie-Bridgeman, … equations,

can Mother Nature provide a universal real gas equation of state?

Hint. Notice:

- T_c, p_c, and V_{mc} for different gases vary widely
- but Z_c is nearly constant (important later).

another hint …

Evaluation of van der Waals *a*, *b* parameters from Critical Data

On the critical isotherm ($T = T_c$) at the critical point:

$$\left(\frac{\partial p}{\partial V_m}\right)_{T=T_c} = 0$$

$$\left(\frac{\partial^2 p}{\partial V_m{}^2}\right)_{T=T_c} = 0$$

Substitute p into these equations from the van der Waals equation

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Evaluation of van der Waals *a*, *b* parameters from Critical Data

at T_c, p_c, and V_mc :

$$\frac{\partial}{\partial V_\mathrm{m}}\left(\frac{RT}{V_\mathrm{m}-b} - \frac{a}{V_\mathrm{m}^2}\right)_{T=T_\mathrm{c}} = 0$$

$$\frac{\partial^2}{\partial V_\mathrm{m}^2}\left(\frac{RT}{V_\mathrm{m}-b} - \frac{a}{V_\mathrm{m}^2}\right)_{T=T_\mathrm{c}} = 0$$

differentiate to get:

$$-\frac{RT_\mathrm{c}}{\left(V_\mathrm{mc}-b\right)^2} + \frac{2a}{V_\mathrm{mc}^3} = 0 \qquad \textbf{Eq (I)}$$

$$\frac{2RT_\mathrm{c}}{\left(V_\mathrm{mc}-b\right)^3} - \frac{6a}{V_\mathrm{mc}^4} = 0 \qquad \textbf{Eq (II)}$$

Evaluation of van der Waals *a*, *b* parameters from Critical Data

Divide Eq (I) by Eq (II)

$$\frac{1}{2}(V_{\mathrm{mc}} - b) = \frac{V_{\mathrm{mc}}}{3}$$

$$\boxed{V_{\mathrm{mc}} = 3b}$$

Substitute $V_{\mathrm{mc}} = 3b$ into Eq (I), get

$$\boxed{T_{\mathrm{c}} = \frac{8}{27R}\frac{a}{b}}$$

Eq (III)

Then

$$p_{\mathrm{c}} = \frac{RT_{\mathrm{c}}}{V_{\mathrm{mc}} - b} - \frac{a}{V_{\mathrm{mc}}^2} = \frac{R8a}{27Rb}\frac{1}{3b - b} - \frac{a}{(3b)^2}$$

Gives

$$\boxed{p_{\mathrm{c}} = \frac{a}{27b^2}}$$

Eq (IV)

Evaluation of van der Waals *a*, *b* parameters from Critical Data

Using thermometers and pressure gauges, T_c and p_c can usually be measured more precisely than V_mc.

Solving Eq (III) and Eq (IV), the van der Waals a and b parameters in terms of T_c and p_c are

$$\boxed{a = \frac{27R^2T_c^2}{64p_\mathrm{c}}} \qquad \boxed{b = \frac{RT_\mathrm{c}}{8p_\mathrm{c}}}$$

Evaluation of van der Waals *a*, *b* parameters from Critical Data

Just a mathematical exercise? **No!**

Important results (***including a Nobel Prize for Prof. van der Waals***).

Example The critical compression factor Z_c for a van der Waals gas is

$$\boxed{Z_c = \frac{p_c V_{mc}}{R T_c} = \frac{\left(\frac{a}{27b^2}\right)(3b)}{R\left(\frac{8a}{27bR}\right)} = \frac{3}{8}}$$

Only an approximate result. But the **$Z_c = 3/8$** prediction suggests

all gases behave "similarly" at the critical point

Law of Corresponding States

p-V-T calculations use **arbitrary "human-defined" units:**

- pressure in bars, Pa, atm, …
- volume in liters, mL, m^3, …
- temperature in K, °C, °F, …

If gases behave similarly at critical points, instead of using arbitrary units, why not try **natural units** for each gas:

- pressure in units of p_c
- volume in units of V_{mc}
- temperature in units of T_c

Reduced Pressure, Temperature and Pressure

reduced pressure $p_\mathrm{r} = \dfrac{p}{p_\mathrm{c}}$

reduced volume $V_\mathrm{r} = \dfrac{V_\mathrm{m}}{V_\mathrm{mc}}$

reduced temperature $T_\mathrm{r} = \dfrac{T}{T_\mathrm{c}}$

$p = p_\mathrm{c}\, p_\mathrm{r}$ $T = T_\mathrm{c}\, T_\mathrm{r}$ $V_\mathrm{m} = V_\mathrm{mc}\, V_\mathrm{r}$

Law of Corresponding States

Example. Calculate the temperature and pressure of CO_2 corresponding to CH_4 at 200 K and 50.0 bar.

Data

CO_2 $T_c = 304.13$ K $p_c = 73.75$ bar

CH_4 $T_c = 190.56$ K $p_c = 45.99$ bar

For CH_4 at 200 K and 50.0 bar:

$T_r = 200 \text{ K} / 190.56 \text{ K} = 1.050$

$p_r = 50.0 \text{ bar} / 45.99 \text{ bar} = 1.088$

For CO_2 at the corresponding state ($T_r = 1.050$, $p_r = 1.088$):

$T = T_r \times T_c = 1.050 \times 304.13 \text{ K} = 319.3 \text{ K}$

$p = p_r \times p_c = 1.088 \times 73.75 \text{ bar} = 80.24 \text{ bar}$

Reduced van der Waals Equation

Substitute $p = p_c p_r$ $V_m = V_{mc} V_r$ $T = T_c T_r$

$$a = \frac{27 R^2 T_c^2}{64 p_c} \qquad b = \frac{R T_c}{8 p_c}$$

into the van der Waals equation $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$

$$p_c p_r = \frac{R T_c T_r}{V_{mc} V_r - \dfrac{R T_c}{8 p_c}} - \frac{\left(\dfrac{27 R^2 T_c^2}{64 p_c}\right)}{V_{mc}^2 V_r^2}$$

Reduced van der Waals Equation

$$p_\mathrm{r} = \frac{T_\mathrm{r}}{\frac{p_\mathrm{c}V_\mathrm{mc}}{RT_\mathrm{c}}V_\mathrm{r} - \frac{1}{8}} - \frac{27}{64}\frac{R^2T_\mathrm{c}^2}{p_\mathrm{c}^2V_\mathrm{mc}^2}\frac{1}{V_\mathrm{r}^2}$$

finally, use $Z_\mathrm{c} = \frac{p_\mathrm{c}V_\mathrm{mc}}{RT_\mathrm{c}} = \frac{3}{8}$ to get

$$\boxed{p_\mathrm{r} = \frac{8}{3}\frac{T_\mathrm{r}}{V_\mathrm{r} - \frac{1}{3}} - \frac{3}{V_\mathrm{r}^2}}$$

Significance

- same reduced equation for all gases
- no "human-defined" units
- no gas-specific *a* or *b* parameters
- no "human-defined" constants (*e.g.*, *R*)

Law of Corresponding States

- the van der Waals equation is not always accurate, especially near the critical point and liquid + vapor region

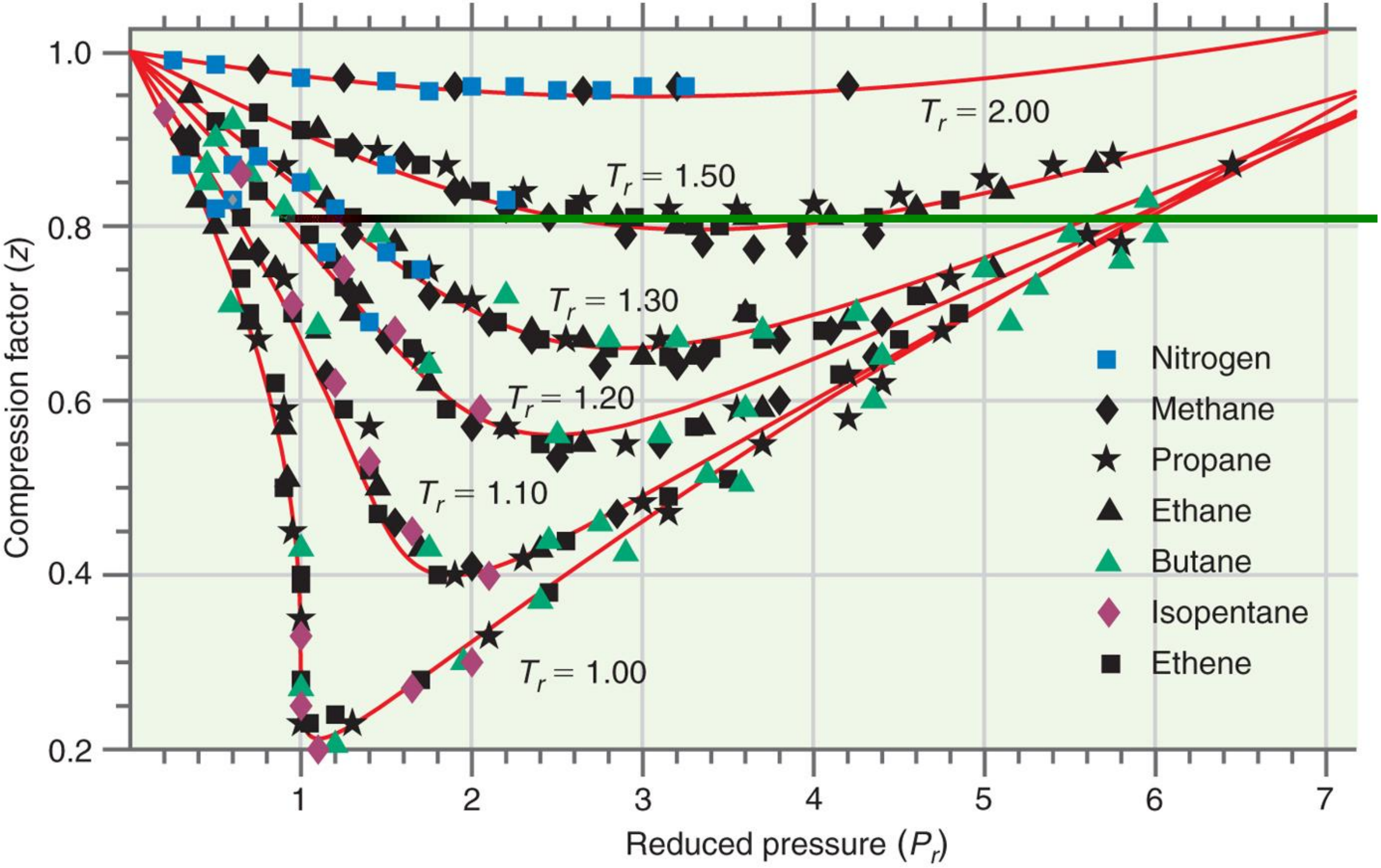
- OK, but the reduced van der Waals equation suggests different gases have similar ("corresponding") properties at identical values of the scaled variables: $p_r \quad V_r \quad T_r$

Is there a "universal" equation of state for real gases?

Try plotting compression factors as a function of reduced temperature and pressure.

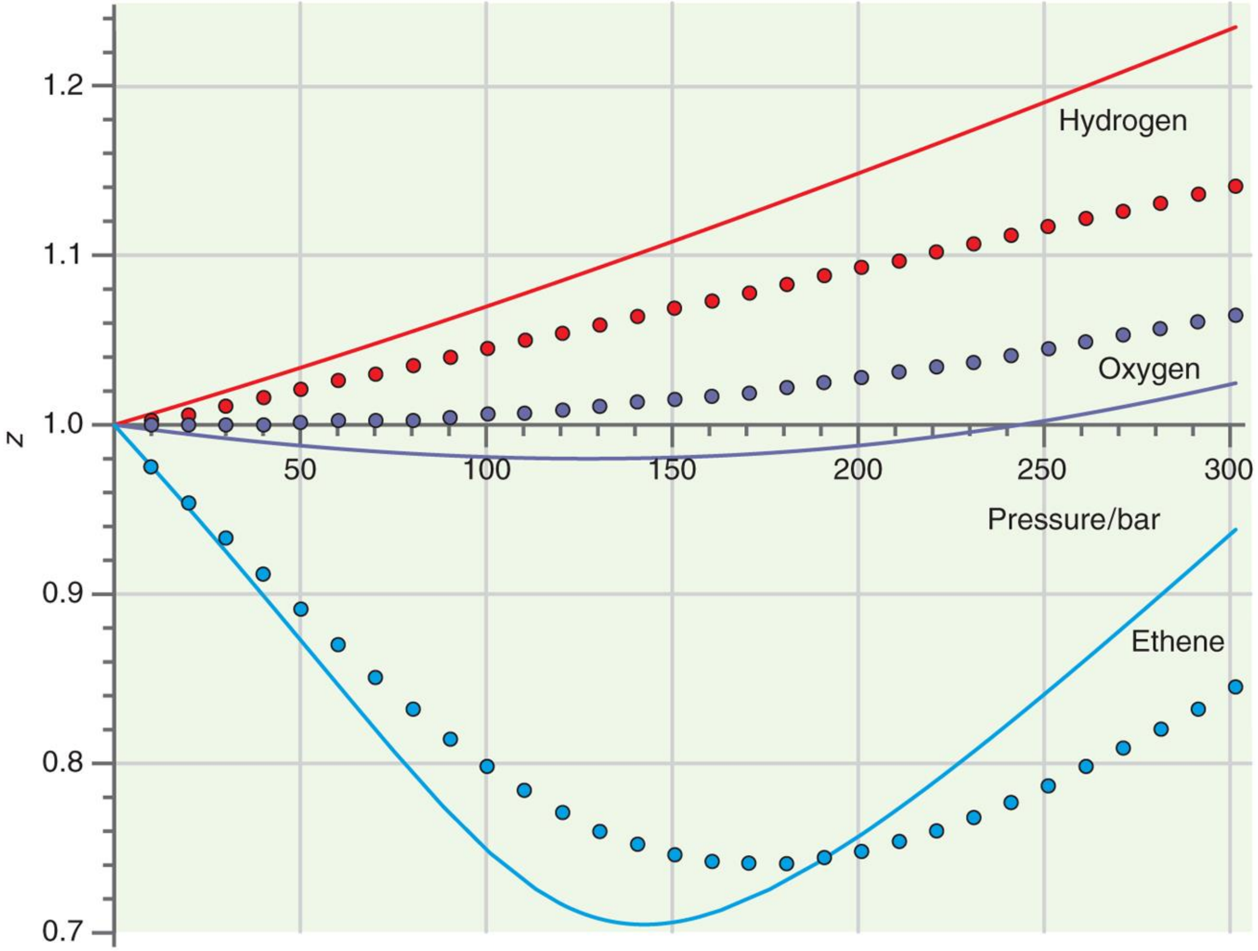
Success !

Compression Factors for Different Gases as a Function of Reduced Pressure and Temperature



Comparison Z values plotted for non-reduced p and T are "all over the place". No apparent pattern. Example:

Compression Factors at 400 K for H_2, O_2 and Ethylene



Section 7.5 Gibbs Energies, Chemical Potentials and Equilibrium Constants for Real Gases

(no testing on material in this Section)

- many physical and chemical processes occur at fixed T, p

- $\Delta G_{T,p} \leq 0$ predicts spontaneous and equilibrium processes under these conditions

- Last Chapter, changes in the Gibbs energy and chemical potential (Gibbs energy per mole) were calculated for ideal gases

- **Important:** How are the Gibbs energy and chemical potential of nonideal **real gases** altered by molecular interactions?

Gibbs Energy of an Ideal Gas

Recall **d*G* = –*S*d*T* + *V*d*p*** for the Gibbs energy gives

$$\left(\frac{\partial G_\mathrm{m}}{\partial p}\right)_T = V_\mathrm{m}$$

$$G_\mathrm{m}(T,p) = G_\mathrm{m}^\mathrm{o}(T,p^\mathrm{o}) + \int_{p^\mathrm{o}}^{p}\left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p = G_\mathrm{m}^\mathrm{o}(T,p^\mathrm{o}) + \int_{p^\mathrm{o}}^{p} V_\mathrm{m}\,\mathrm{d}p$$

For an **ideal gas** **(V_m = RT/p)** :

$$G_\mathrm{m}^\mathrm{ideal}(T,p) = G_\mathrm{m}^\mathrm{o}(T,p^\mathrm{o}) + \int_{0}^{p}\frac{RT}{p}\,\mathrm{d}p$$

$$\boxed{G_\mathrm{m}^\mathrm{ideal}(T,p) = G_\mathrm{m}^\mathrm{o}(T,p^\mathrm{o}) + RT\ln(p/p^\mathrm{o})}$$

ideal gas

Gibbs Energy of a Real Gas – the Fugacity

For a **real gas** **($V_m = ZRT/p$)** , Lewis suggested keeping the same mathematical form as the expression for $G_\mathrm{m}^{\mathrm{ideal}}$ by **replacing the pressure p with the fugacity f**.

$$\boxed{\begin{aligned} G_\mathrm{m}^{\mathrm{real}}(T,p) &= G_\mathrm{m}^{\mathrm{o}}(T,p^{\mathrm{o}}) + RT\ln(f/p^{\mathrm{o}}) \\ &= G_\mathrm{m}^{\mathrm{o}}(T,p^{\mathrm{o}}) + RT\ln(\gamma\, p/p^{\mathrm{o}}) \end{aligned}}$$

real gas

The **fugacity coefficient** γ is correction factor applied to the pressure to give the fugacity.

All gases are ideal as the pressure drops to zero:

$$f \to p \quad \text{as} \quad p \to 0$$

$$\gamma \to 1 \quad \text{as} \quad p \to 0$$

Fugacity Calculations for Nonideal Gases

$$G_{\mathrm{m}}^{\mathrm{real}}(T,p) - G_{\mathrm{m}}^{\mathrm{ideal}}(T,p) = G_{\mathrm{m}}^{\mathrm{o}}(T,p^{\mathrm{o}}) + RT\ln(f/p^{\mathrm{o}}) - G_{\mathrm{m}}^{\mathrm{o}}(T,p^{\mathrm{o}}) + RT\ln(p/p^{\mathrm{o}})$$

$$\boxed{G_{\mathrm{m}}^{\mathrm{real}}(T,p) - G_{\mathrm{m}}^{\mathrm{ideal}}(T,p) = RT\ln(f/p) = RT\ln(\gamma)}$$

$$G_{\mathrm{m}}^{\mathrm{real}}(T,p) - G_{\mathrm{m}}^{\mathrm{ideal}}(T,p) = \left(\cancel{G_{\mathrm{m}}^{\mathrm{real}}(T,0)} + \int_0^p V_{\mathrm{m}}^{\mathrm{real}}\,\mathrm{d}p\right) - \left(\cancel{G_{\mathrm{m}}^{\mathrm{ideal}}(T,0)} + \int_0^p V_{\mathrm{m}}^{\mathrm{ideal}}\,\mathrm{d}p\right)$$

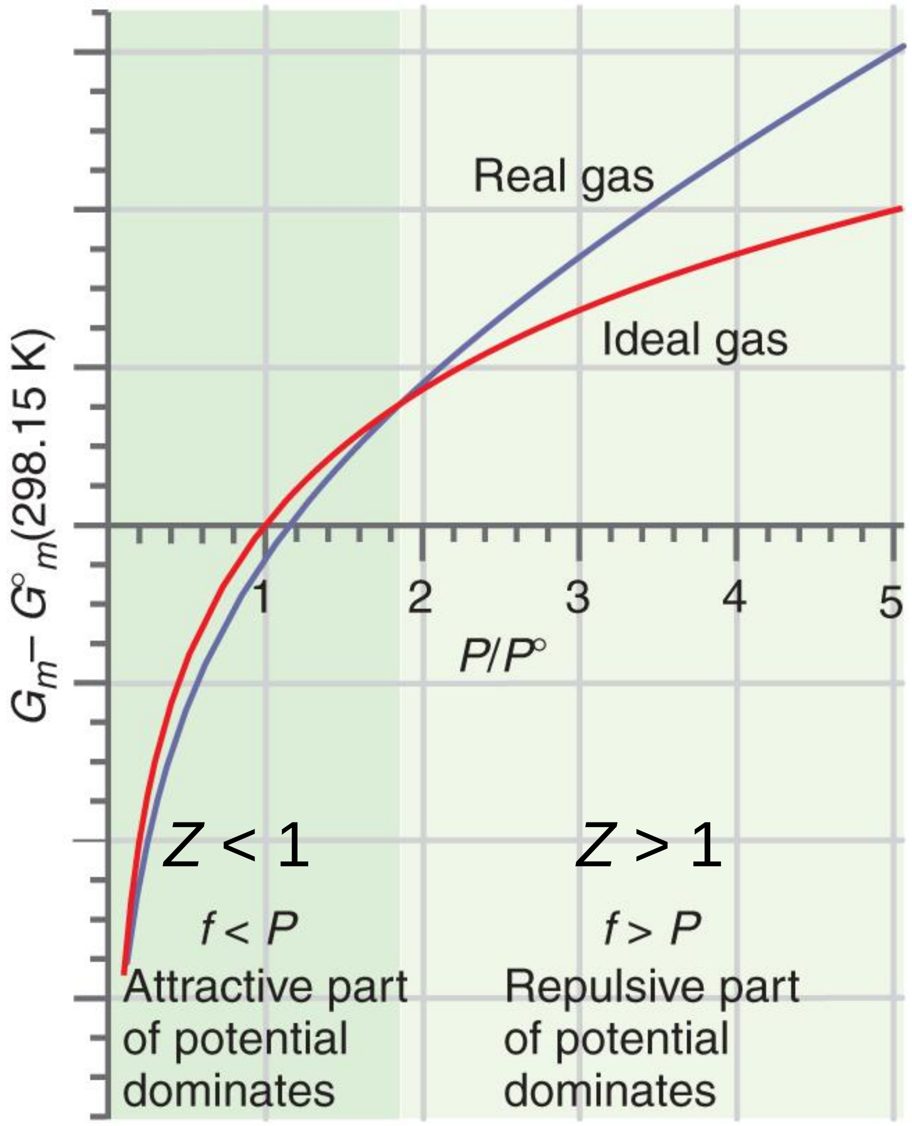
gases ideal in the limit $p \to 0$

$$V_{\mathrm{m}}^{\mathrm{ideal}} = \frac{RT}{p}$$

$$G_{\mathrm{m}}^{\mathrm{real}}(T,p) - G_{\mathrm{m}}^{\mathrm{ideal}}(T,p) = \int_0^p \left(V_{\mathrm{m}}^{\mathrm{real}} - \frac{RT}{p}\right)\mathrm{d}p = \int_0^p \frac{RT}{p}\left(\frac{pV_{\mathrm{m}}^{\mathrm{real}}}{RT} - 1\right)\mathrm{d}p$$

$$\boxed{G_{\mathrm{m}}^{\mathrm{real}}(T,p) - G_{\mathrm{m}}^{\mathrm{ideal}}(T,p) = RT\int_0^p \frac{Z-1}{p}\,\mathrm{d}p = RT\ln(f/p) = RT\ln(\gamma)}$$

Gibbs Energies of Real and Ideal Gases



$$G_{\mathrm{m}}^{\mathrm{real}} - G_{\mathrm{m}}^{\mathrm{ideal}} = \int_0^p \frac{Z-1}{p}\,\mathrm{d}p$$

at high pressures

$$G_{\mathrm{m}}^{\mathrm{real}} > G_{\mathrm{m}}^{\mathrm{ideal}}$$

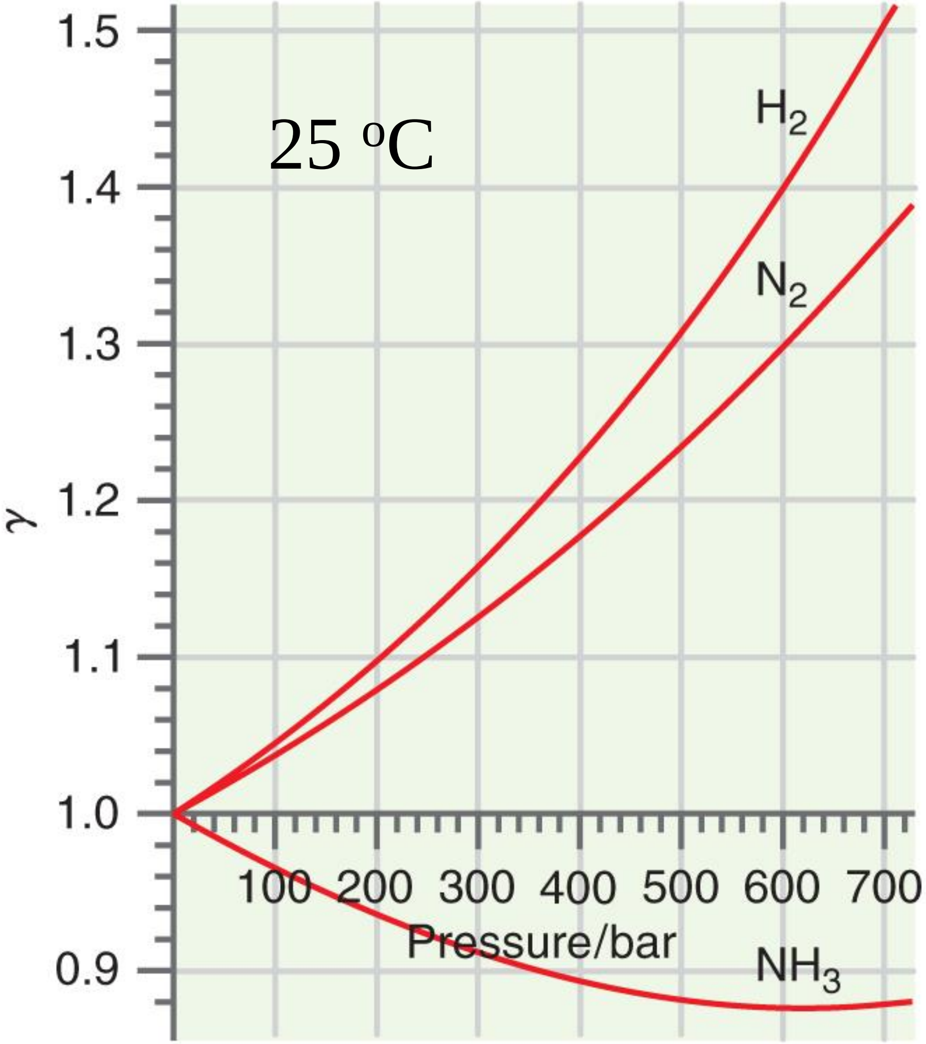
at moderate pressures

$$G_{\mathrm{m}}^{\mathrm{real}} < G_{\mathrm{m}}^{\mathrm{ideal}}$$

in the limit $p \rightarrow 0$

$$G_{\mathrm{m}}^{\mathrm{real}} = G_{\mathrm{m}}^{\mathrm{ideal}}$$

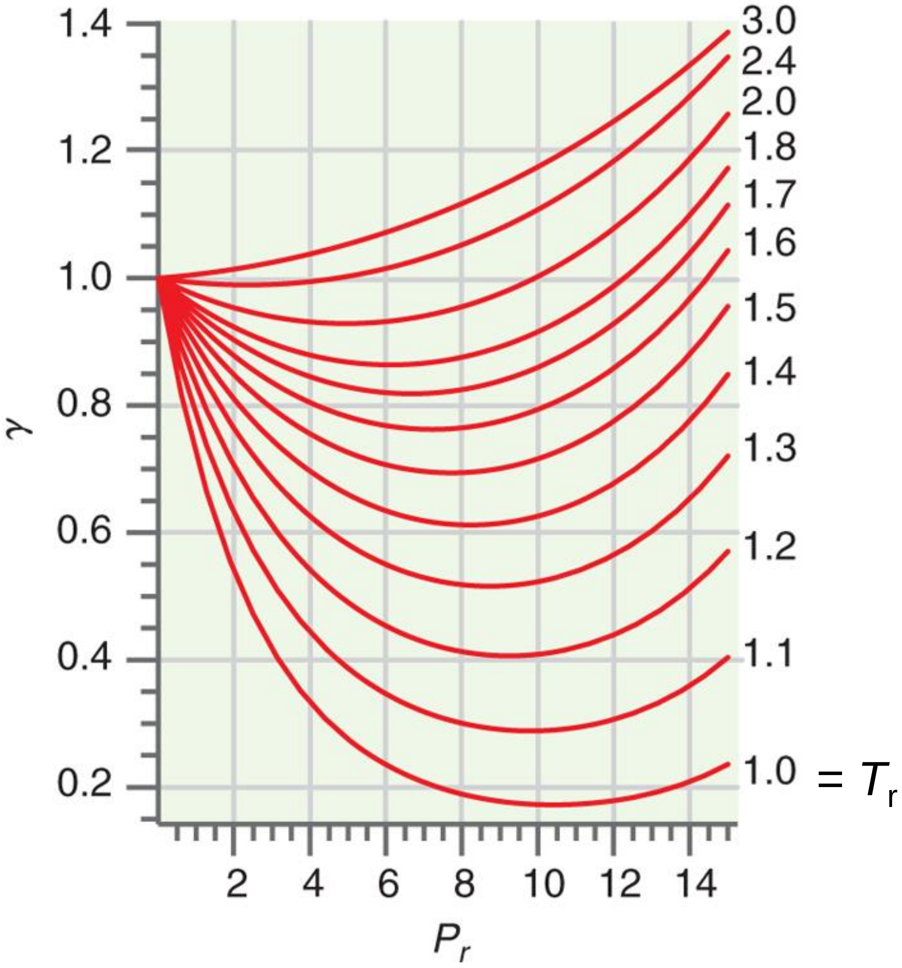
Fugacity Coefficient $\gamma = f/p$

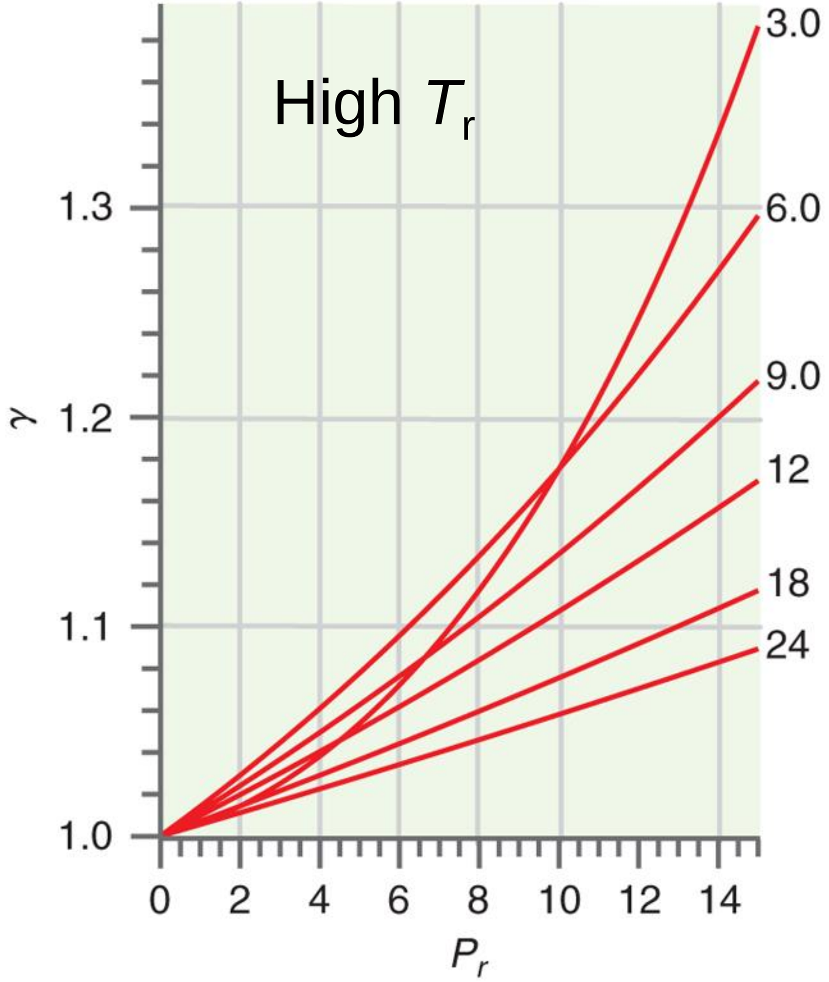


$$\begin{aligned} G_m^{\text{real}} - G_m^{\text{ideal}} &= RT\ln(f/p) \\ &= RT\ln\gamma \end{aligned}$$

Fugacity Coefficients from Corresponding States

$$\ln\gamma = \int_0^p \frac{Z-1}{p}\,\mathrm{d}p$$





Important **Chemical Applications** of the Fugacity

Example Chemical equilibrium for the famous ammonia synthesis reaction

$$\mathbf{N_2(g) + 3\,H_2(g) \leftrightarrow 2\,NH_3(g)}$$

is usually written **for ideal gases** as

$$K = \frac{(p_{\mathrm{NH3}}/p^{\mathrm{o}})^2}{(p_{\mathrm{N2}}/p^{\mathrm{o}})(p_{\mathrm{H2}}/p^{\mathrm{o}})^3}$$

or

$$K = \frac{(p_{\mathrm{NH3}})^2}{p_{\mathrm{N2}}\,(p_{\mathrm{H2}})^3}$$

But wait !

Important Chemical Applications of the Fugacity

Ammonia is produced industrially **(a billion-dollar business)**
at hundreds of bars pressures, where the gases are strongly nonideal.

Ammonia yields calculated assuming ideal gases can be in error
by orders of magnitude.

Ammonia production plants (and many other industrial processes)
are designed and operated using fugacities.

$$K = \frac{(f_{\mathrm{NH3}})^2}{f_{\mathrm{N2}}\,(f_{\mathrm{H2}})^3} \qquad \left(\text{not} \qquad K = \frac{(p_{\mathrm{NH3}})^2}{p_{\mathrm{N2}}\,(p_{\mathrm{H2}})^3}\right)$$

Chemical Potential

The Gibbs energy per mole of a substance (G_m) is frequently called chemical potential (μ).

For a **pure substance:**

$$\boxed{\mu = G_\mathrm{m} = \frac{G}{n}}$$

Chemical potential of substance *i* in a **mixture:**

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{k\neq i}}}$$

For an **ideal gas**: $\mu_i = \mu_i^\mathrm{o} + RT\ln(p_i/p^\mathrm{o})$

For an **real gas**: $\mu_i = \mu_i^\mathrm{o} + RT\ln(f_i/p^\mathrm{o})$

Often abbreviated: $\mu_i = \mu_i^\mathrm{o} + RT\ln p_i$

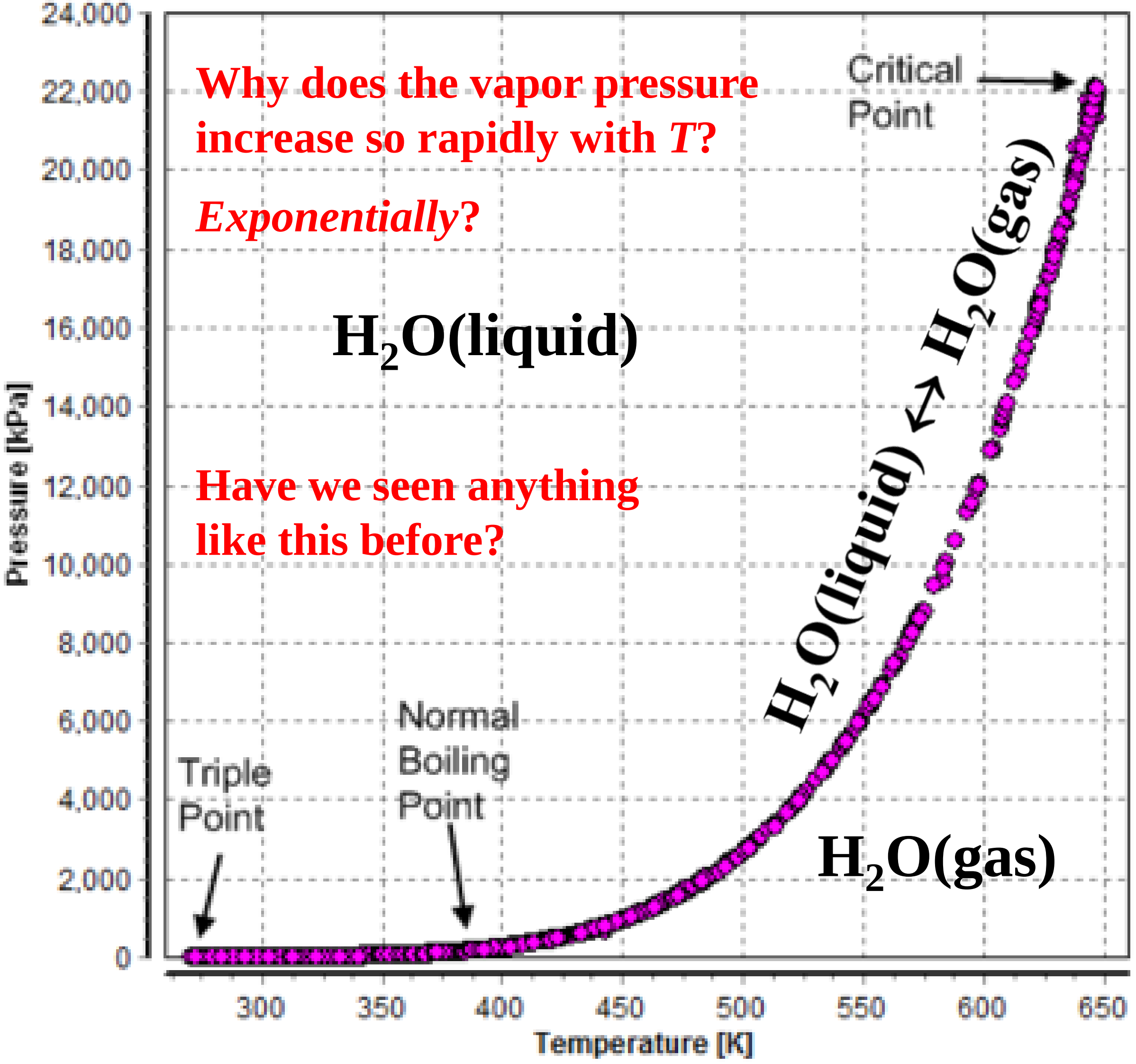
$$\mu_i = \mu_i^\mathrm{o} + RT\ln f_i$$

Chapter 8. Phase Diagrams and the Stability of Solids, Liquids and Gases

Summary

- phase diagrams are used to provide graphical representations of conditions required for the existence of solids, liquids or vapors
- the stability of different phases is related to changes in the Gibbs energy with temperature and pressure
- the **phase rule** is introduced to predict the number of different phases that can co-exist at equilibrium
- the effects of **surface tension** at the boundary between phases are introduced

Vapor Pressure Phase Diagram for Water



Why does the vapor pressure increase so rapidly with *T*?

***Exponentially*?**

Have we seen anything like this before?

$H_2O(\text{liquid}) \quad = \quad H_2O(\text{gas})$

Equilibrium constant $K = p_{H2O}$

Data at 25 ^{o}C:

$$\Delta H^{o} = \Delta H_{fm}{}^{o}(H_20,\ g) - \Delta H_{fm}{}^{o}(H_20,\ l)$$
$$= -241{,}818\ \text{J mol}^{-1} - (-285{,}830\ \text{J mol}^{-1})$$
$$= 44{,}012\ \text{J mol}^{-1}$$

$$\Delta G^{o} = \Delta G_{fm}{}^{o}(H_20,\ g) - \Delta G_{fm}{}^{o}(H_20,\ l)$$
$$= -228{,}572\ \text{J mol}^{-1} - (-237{,}129\ \text{J mol}^{-1})$$
$$= 8{,}557\ \text{J mol}^{-1}$$

$$K = \exp(-\Delta G^{o}/RT) = p_{H2O} = 0.0317\ \text{bar}$$

H_2O(liquid) = H_2O(gas)

Temperature Dependence of K and p_{H2O} ?

van’t Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln p_{H2O}}{\mathrm{d}(1/T)} = -\frac{\Delta H^{o}}{R} \approx \text{constant}$$

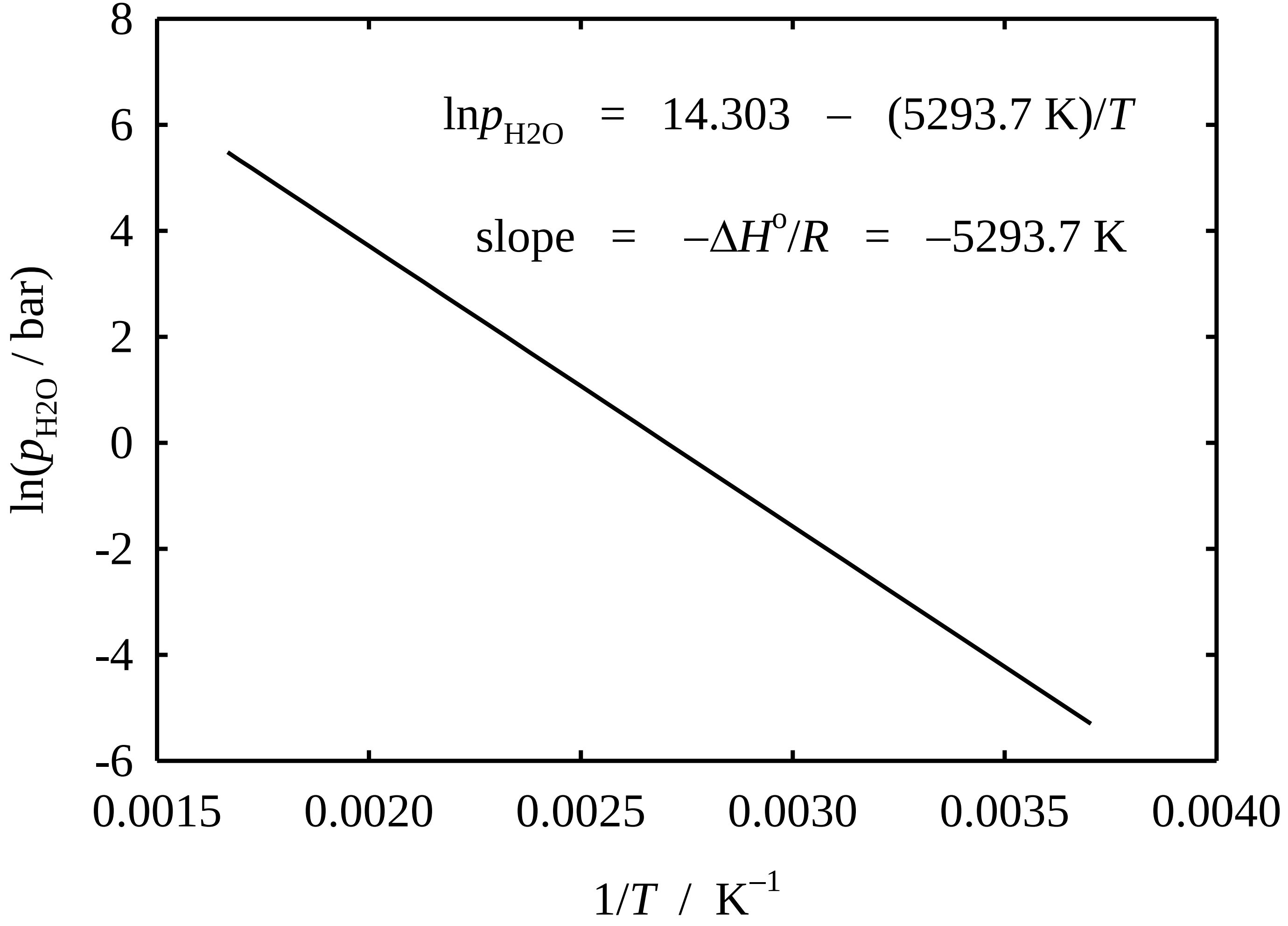
$$\mathrm{d}\ln p_{H2O} = -\frac{\Delta H^{o}}{R}\,\mathrm{d}\frac{1}{T}$$

Integrate:

$$\ln p_{H2O}(T) - \ln p_{H2O}(298.15\text{ K}) = -\frac{\Delta H^{o}}{R}\left(\frac{1}{T} - \frac{1}{298.15\text{ K}}\right)$$

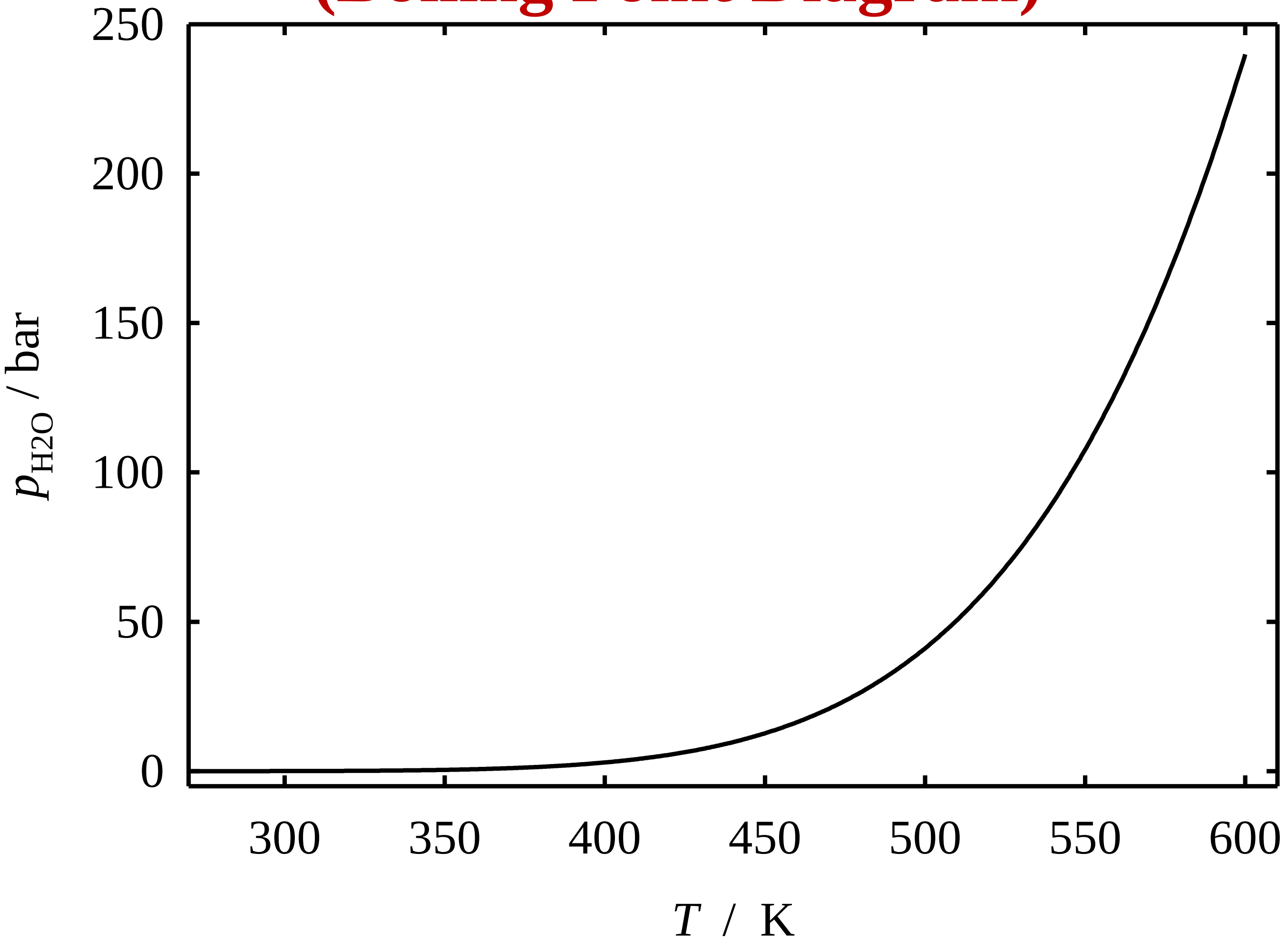
H_2O(liquid) = H_2O(gas)

lnp_{H2O} plotted against 1/T (linear)



H_2O(liquid) = H_2O(gas)

p_{H2O} plotted against T (exponential in 1/T) (Boiling Point Diagram)

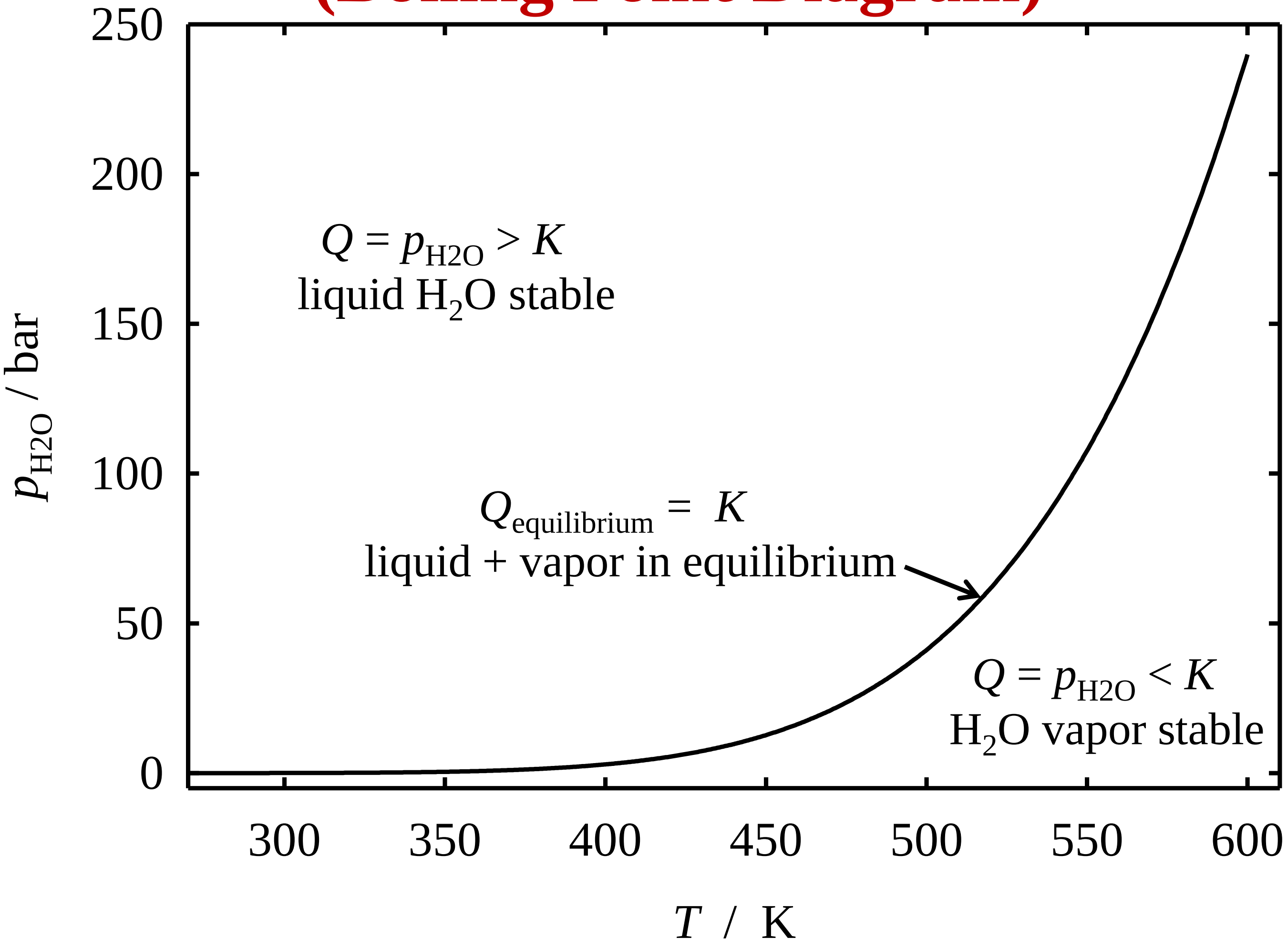


H_2O(liquid) = H_2O(gas)

$K = p_{H2O}$

p_{H2O} plotted against T (exponential in $1/T$)

(Boiling Point Diagram)



$$H_2O(\text{liquid}) \quad = \quad H_2O(\text{gas})$$

$$K = p_{H2O}$$

This example shows:

<u>phase-diagram regions</u> indicate phases present

<u>phase-diagram lines</u> indicate phases co-existing at equilibrium

<u>phase-diagram lines</u> can provide quantitative thermodynamic data (*e.g.*, enthalpy of vaporization)

Section 8.1 Stability of Solid, Liquid and Gas Phases

What is a “Phase” ?

A form of matter with uniform chemical composition and uniform physical properties (such as density).

example ice (solid water)

Experience suggests:

- solid phases exist at low temperatures
- heating a solid can convert it to a liquid
- heating a liquid converts it to a gas

Relative Stability of Different Phases

How does a **temperature change** affect the stability of a phase?

From $\mathbf{d\mu = dG_m = -S_m dT + V_m dp}$, the change in the chemical potential (Gibbs energy per mole) with temperature is

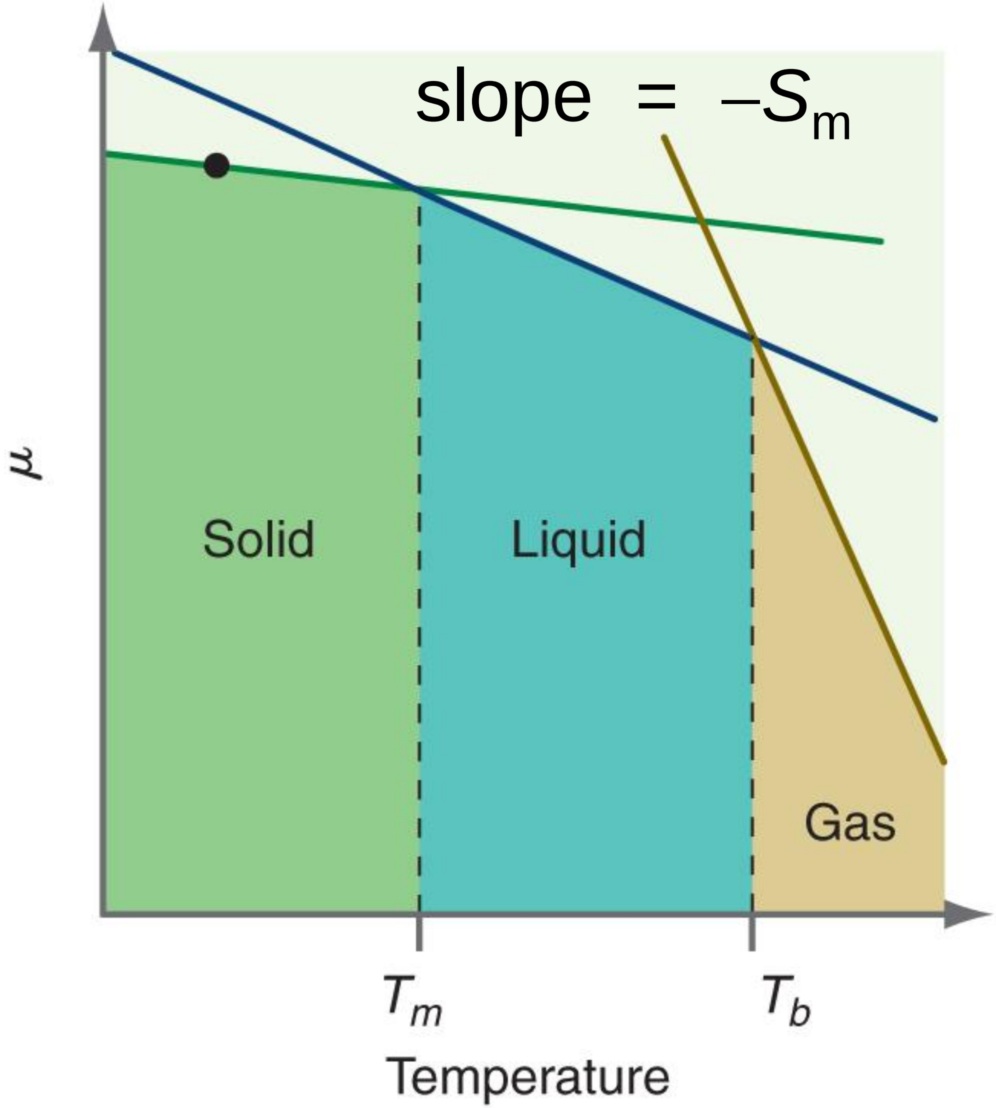
$$\boxed{\left(\frac{\partial \mu}{\partial T}\right)_p = \left(\frac{\partial G_\mathrm{m}}{\partial T}\right)_p = -S_\mathrm{m}}$$

The relative **molar entropies**

$$S_\mathrm{m}(\text{solid}) < S_\mathrm{m}(\text{liquid}) < S_\mathrm{m}(\text{gas})$$

indicate that the chemical potential of the gaseous form of a substance is most sensitive to temperature.

Relative Stability of Different Phases



$T < T_m$ (melting point)
solid most stable
(μ_{solid} lowest)

$T_m < T < T_b$
liquid most stable
(μ_{liquid} lowest)

$T > T_b$ (boiling point)
gas most stable
(μ_{gas} lowest)

Relative Stability of Different Phases

How does a **pressure change** affect the stability of a phase?

From $\mathbf{d\mu = dG_m = -S_m dT + V_m dp}$, the change in the chemical potential (Gibbs energy per mole) with pressure is

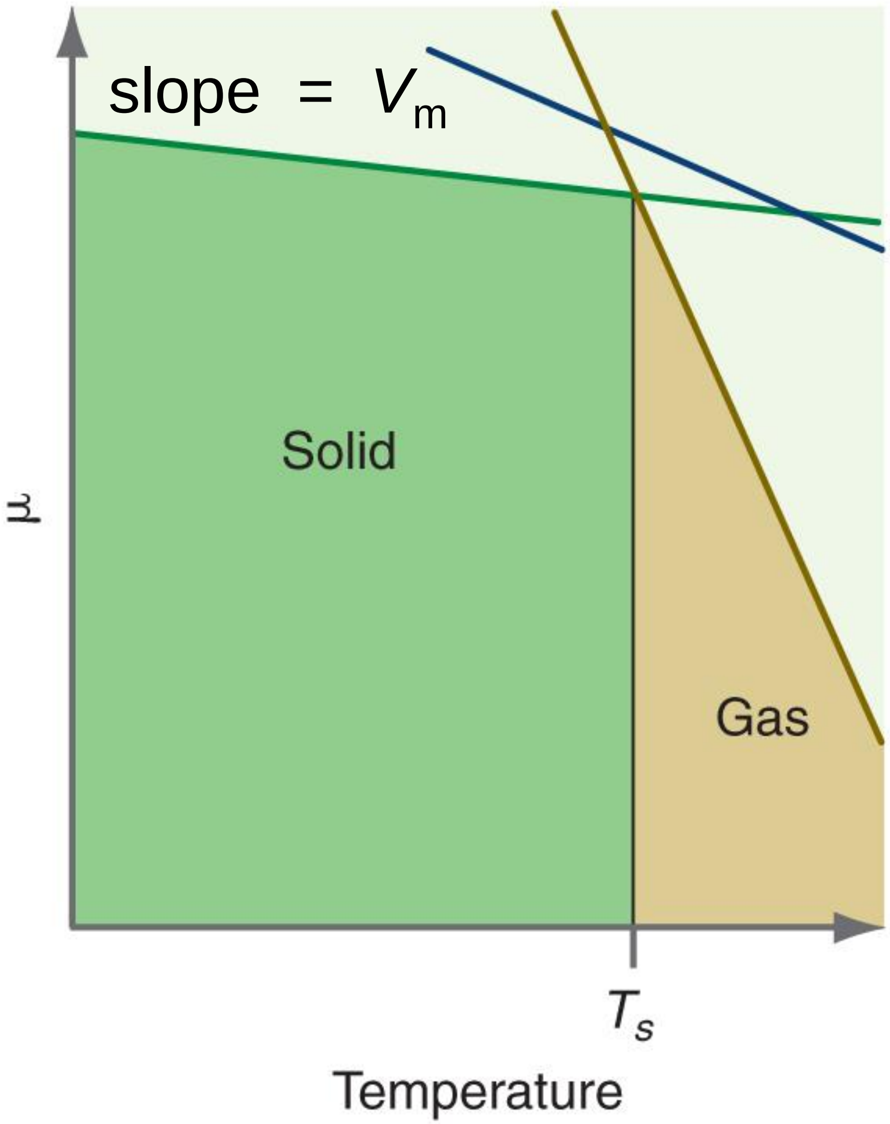
$$\boxed{\left(\frac{\partial \mu}{\partial p}\right)_T = \left(\frac{\partial G_\mathrm{m}}{\partial p}\right)_T = V_\mathrm{m}}$$

The relative **molar volumes**

$V_\mathrm{m}(\text{solid}) \ll V_\mathrm{m}(\text{gas})$ $\qquad$ $V_\mathrm{m}(\text{liquid}) \ll V_\mathrm{m}(\text{gas})$

suggests that only the chemical potential of the gaseous form of a substance is appreciably affected by pressure changes.

Relative Stability of Different Phases



At sufficiently low pressures, μ_{gas} can drop below μ_{liquid} allowing direct conversion of **solid to gas** **(**sublimation**)** upon heating.

Application: "Dry" Ice

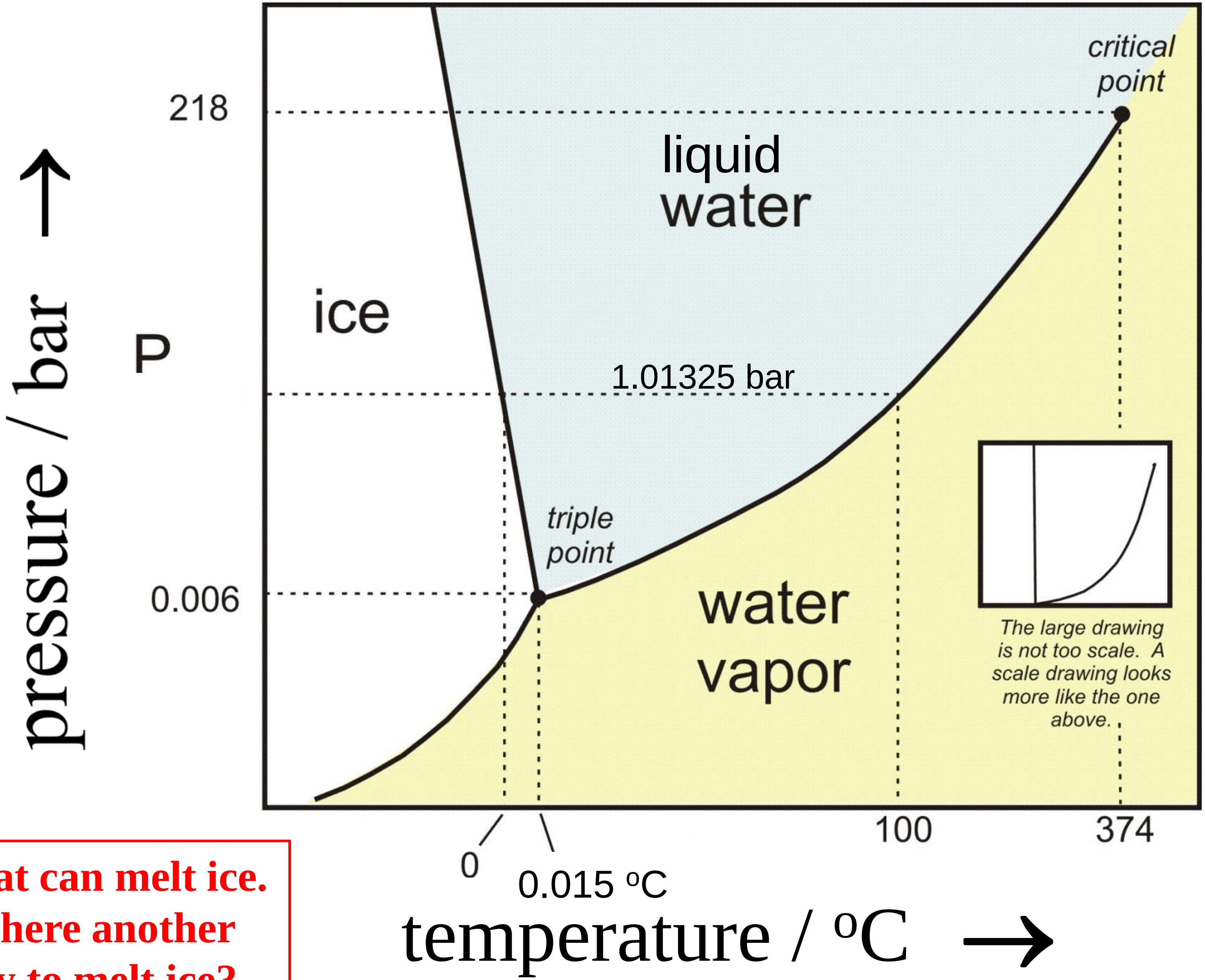
$$\mathbf{CO_2(s) \rightarrow CO_2(g)}$$

A convenient commercial refrigerant that does not form puddles of liquid (like melting ice) that can damage some products.

Section 8.2 Pressure-Temperature Phase Diagrams (for Pure Substances)

- substances can exist as **solids, liquids or gases**
- **what is there** at a given temperature and pressure?
- *p*-*T* phase diagrams provide a convenient **graphical display** of the phase (or phases) present at equilibrium
- *p*-*T* phase diagrams also provide **quantitative information** about enthalpy (and volume) changes for phase transitions
- many **important practical applications**, such as:
    - will we have **rain, snow, dew, or frost ?**
    - **convert graphite to diamond ?**
    - why do **pressure-cookers** work so quickly?
    - why are **high-pressure steam engines** more efficient

Temperature-Pressure Phase Diagram for Water

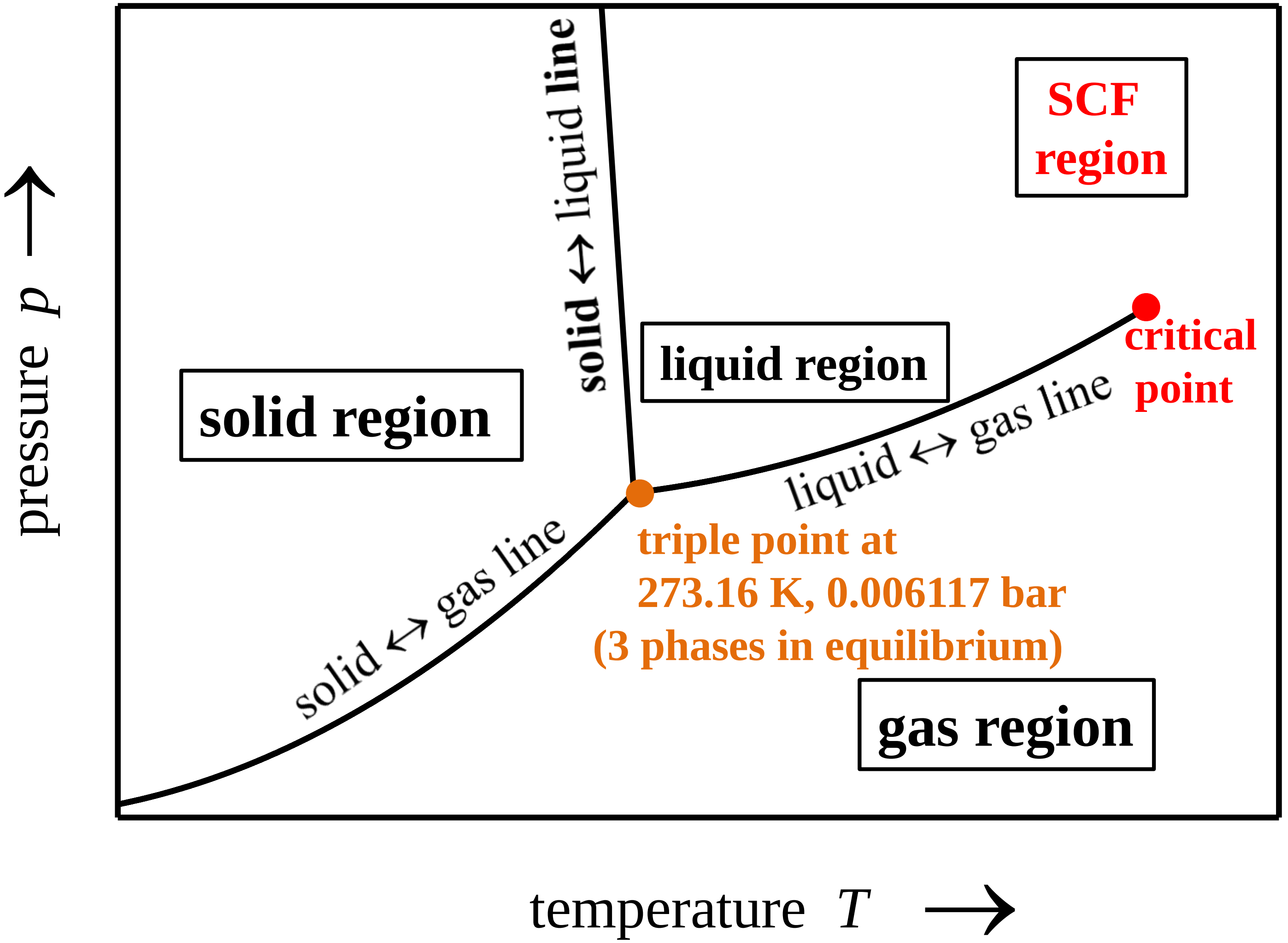


The large drawing is not too scale. A scale drawing looks more like the one above.

- **Heat can melt ice. Is there another way to melt ice?**

Temperature-Pressure Phase Diagram

(pure substance)



SCF
supercritical fluid
($T > T_c$, $p > p_c$)

Why does the liquid-gas line end at the critical point?

Why is the solid-liquid line so steep?

What is the significance of the triple point?

Critical Points and Gas-Liquid-Solid Triple Points

Substance	T_c / K	p_c / bar	T_{tp} / K	p_{tp} / bar
He	5.25	2.27	2.19	0.051
Ne	44.49	26.79	24.57	0.432
Ar	150.86	48.98	83.81	0.689
Kr	209.35	54.3	115.76	0.741
Xe	289.74	58.4	161.3	0.815
H_2	32.98	12.93	13.84	0.0704
O_2	154.58	50.43	54.36	0.00152
N_2	126.20	33.98	63.18	0.126
CO_2	304.13	73.75	216.55	5.17
CH_4	190.56	45.99	90.68	0.117
CH_3CH_3	305.32	48.72	89.89	8.0×10^{-6}
$CH_3CH_2CH_3$	369.83	42.48	85.47	1.7×10^{-6}
H_2O	647.14	220.64	273.16	0.006117
NH_3	405.40	113.53	195.4	0.06076