

Thermodynamics: Phenomenology & Applications

- Work and other forms of energy
- Fundamental Laws of Thermodynamics
- Ideal-gas laws and simple processes
 - Technological applications, cyclic engines
- Real gases equation of state
 - Technological applications
- Phase equilibria, solutions
- Transport phenomena

Reading Assignments

Weeks 13&14

LN V-VI:

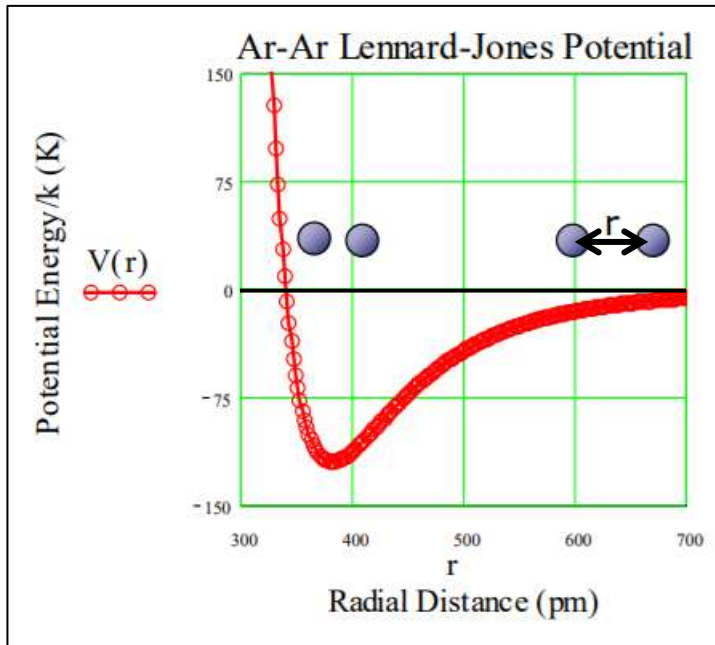
Kondepudi Ch. 3.5-3.7,
6 & 7

Additional Material

McQuarrie & Simon

Ch. 5 & 6

Real Substances



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

Different mutual interactions:

- Coulomb repulsion of atomic nuclei
- Coulomb attraction of ions
- Dipole-dipole interactions (both, qm)
- Vander Waals interaction of atoms

Ideal gas approximation good: $V > 5\text{L/mol}$ (diatomic), $V > 20\text{L/mol}$ (complex)

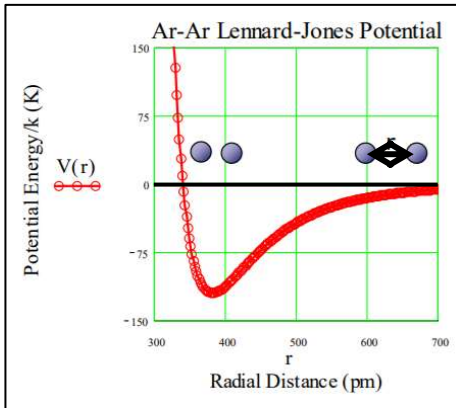
→ Real gas molecules interact with each other → motion is more or less free depending on density, pressure, temperature

→ Different phases of substances:
Low density → gas
High densities (small distances) → liquid or solid behavior.

→ Coexistence of different phases in specific regions density-temperature
Phase transitions can be sudden (fast)

→ EoS non-monotonic → liquid-gas instability, different solid crystal structures.

Effective Density of Real Gases



High densities = small distances) \rightarrow excluded volume

Blocked volume ΔV : not available for another particle
 $\Delta V \rightarrow R_{blocked} = 2 \cdot R \rightarrow 2^3$ times the specific volume,

$$\Delta V = 8 \cdot v \quad \text{with } v = \frac{4\pi}{3} \cdot R^3$$

Effective volume for N particles: $V \rightarrow V_{eff} = V - 8 \cdot N \cdot v$

$$V_{eff} = V \cdot (1 - 8 \cdot \rho \cdot v) < V$$

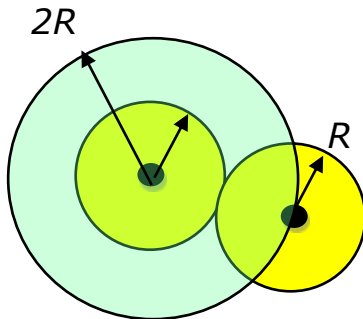
Effective density of real gas: $\rho_{eff} = N/V_{eff}$

$$\rho_{eff} = \frac{N}{(V - 8 \cdot N \cdot v)} = \frac{N}{V} \frac{1}{(1 - 8 \cdot \rho \cdot v)}$$

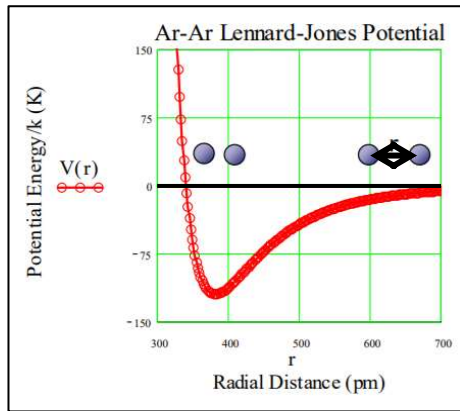
$$\rho = \frac{N}{V} \rightarrow \rho_{eff} = \frac{\rho}{(1 - 8 \cdot \rho \cdot v)} > \rho$$

Excluded Volume

Hard-sphere interactions



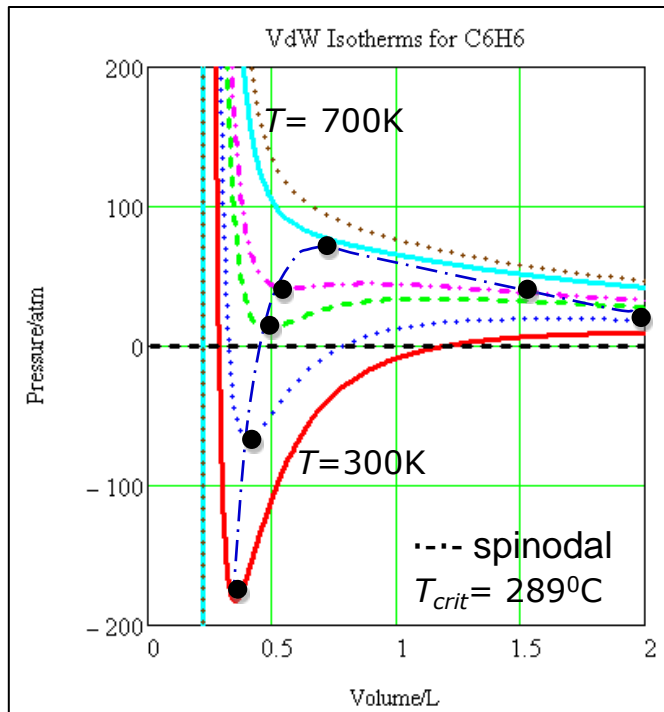
Effective Pressure of Real Gases/ vdW EoS



Without interaction: $\langle E \rangle = (1/2)k_B T$ per *d.o.f.* $\rightarrow K = (3/2)k_B T$
 Long-range part of **L-J** potential = attractive force, retards the motion of the particles $\rightarrow K < (3/2)k_B T \rightarrow p_{\text{real}} < p_{\text{IG}}$

Effective interaction rate volume for N particles: $\sigma \sim \rho^2$

$$\rightarrow \Delta p \propto \rho^2 \rightarrow \Delta p \sim \rho^2 \approx -a \cdot \frac{N^2}{V^2} \text{ with } a > 0$$



Observed pressure for real gas $p_{\text{meas}} < p_{\text{IG}}$

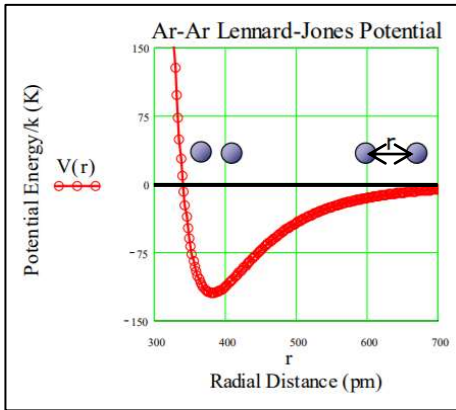
$$p_{\text{meas}} = p_{\text{IG}} - \Delta p$$

$$Nk_B T = p_{\text{IG}} \cdot V_{\text{eff}} = (p_{\text{meas}} - \Delta p) \cdot V \cdot (1 - 8\rho v)$$

$$\left(p + a \left(\frac{N}{V} \right)^2 \right) \cdot (V - Nb) = Nk_B T \quad \text{van der Waals EoS for real gases}$$

Use experimental observables/parameters: p , V
 for fits to vdW EoS

Internal Energy of Real Gases



van der Waals EoS (**linear** function of **T**)

$$p = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2}$$

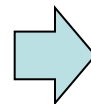
$$\rightarrow \text{potential energy term } a \cdot \left(\frac{n}{V}\right)^2 = a \cdot \rho^2$$

$$U(n, V, T) = U_{IG}(n, V, T) - a \cdot \left(\frac{n}{V}\right)^2 \cdot V < \underline{U_{IG}(n, V, T)}$$

$$U(n, V, T) \xrightarrow{V \rightarrow \infty} U_{IG}(n, V, T)$$

Heat Capacity

$$C_V = C_{V,IG} - \frac{\partial}{\partial T} \left(a \cdot \frac{n^2}{V} \right) = C_{V,IG} + 0$$



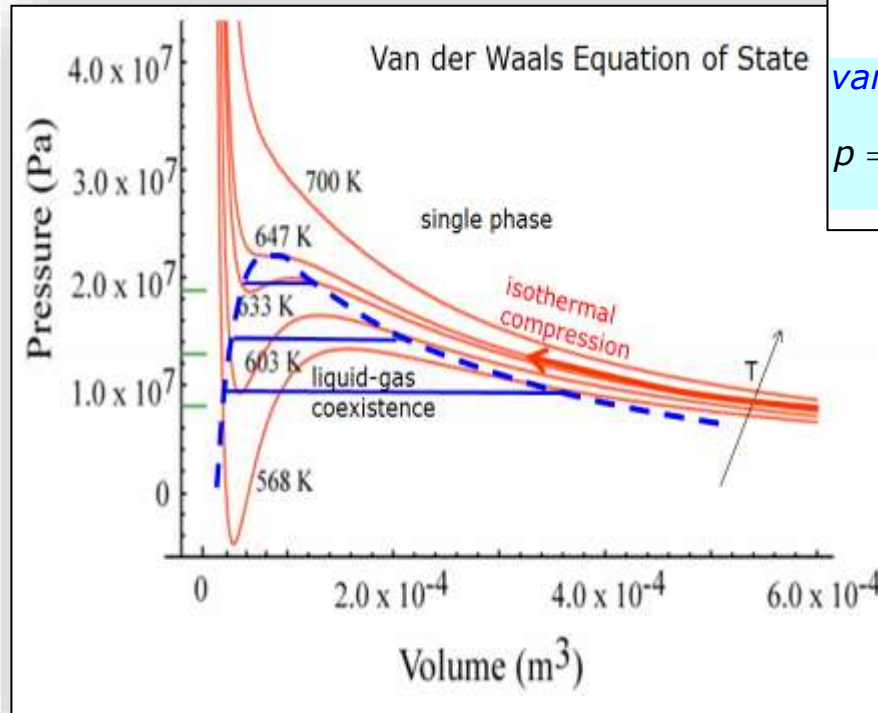
$$C_V^{vdW} = C_{V,IG}$$

$$vdW \text{ EoS} \rightarrow C_p - C_V = \left(\alpha^2 / \kappa_T \right) \cdot V \cdot T$$

Compressibility factor α

Parameterization of Real Gases

Ideal gas approximation good: $V > 5\text{L/mol}$ (diatomic), $V > 20\text{ L/mol}$ (complex)
 Real-gas EoS non-monotonic \rightarrow liquid-gas instability.



Useful Parameterizations

van der Waals EoS :

$$p = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2}$$

Redlich Kwong EoS :

$$p = \frac{n \cdot R \cdot T}{(V - nb)} - \frac{n^2 a}{\sqrt{T}} \cdot \frac{1}{V(V + nb)}$$

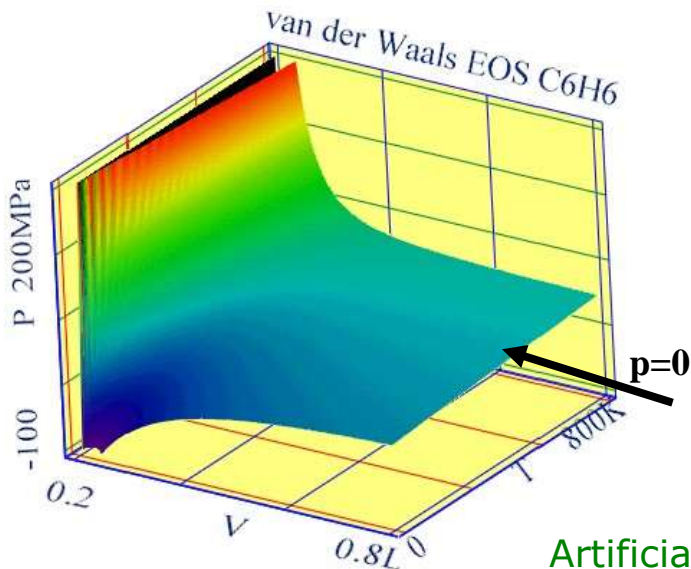
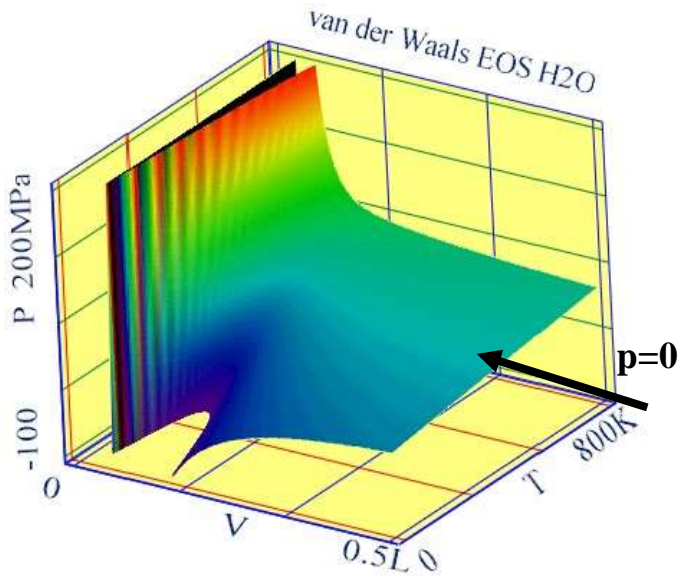
Van der Waals Parameters

Substance	a (L ² atm/mol ²)	b (L/mol)
He	0.0341	0.0237
H ₂	0.244	0.0266
O ₂	1.36	0.0318
H ₂ O	5.46	0.0305
CCl ₄	20.4	0.1383

For higher compression, real (vdW model) gases tend to collapse (p decreases with decreasing V) \rightarrow liquifaction

Correct the EoS for instability (unphysical for single phase): [Maxwell Construction](#)

Real-Gas Equation of State



van der Waals: effects taken into account

- average volume taken by gas particles \rightarrow available volume reduced. \rightarrow parameter ***b***
- collisions between particles reduce the actual pressure, attractive interactions.

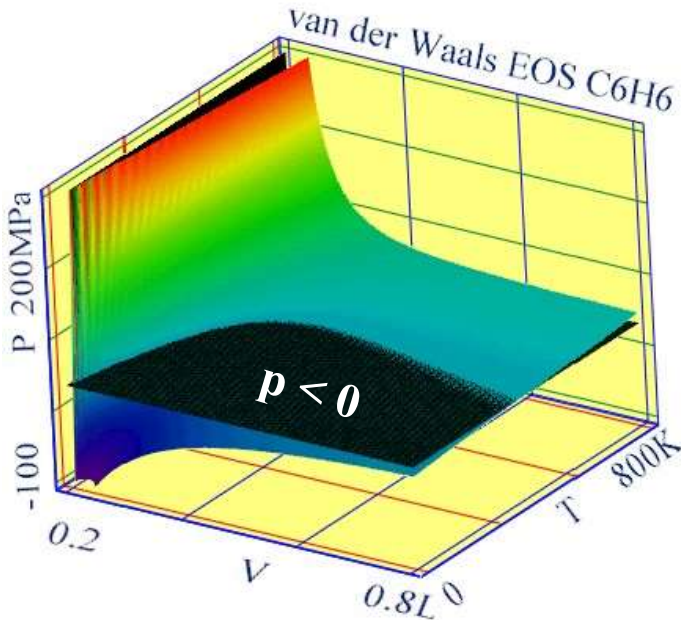
$\rightarrow N_{\text{coll}} \propto (\text{density})^2,$
 \rightarrow scaling parameter ***a***

$$\underbrace{\left(p + a \cdot \left(\frac{n}{V} \right)^2 \right)}_{\hat{=} \text{ideal pressure}} \underbrace{(V - n \cdot b)}_{\hat{=} \text{ideal volume}} = n \cdot R \cdot T$$

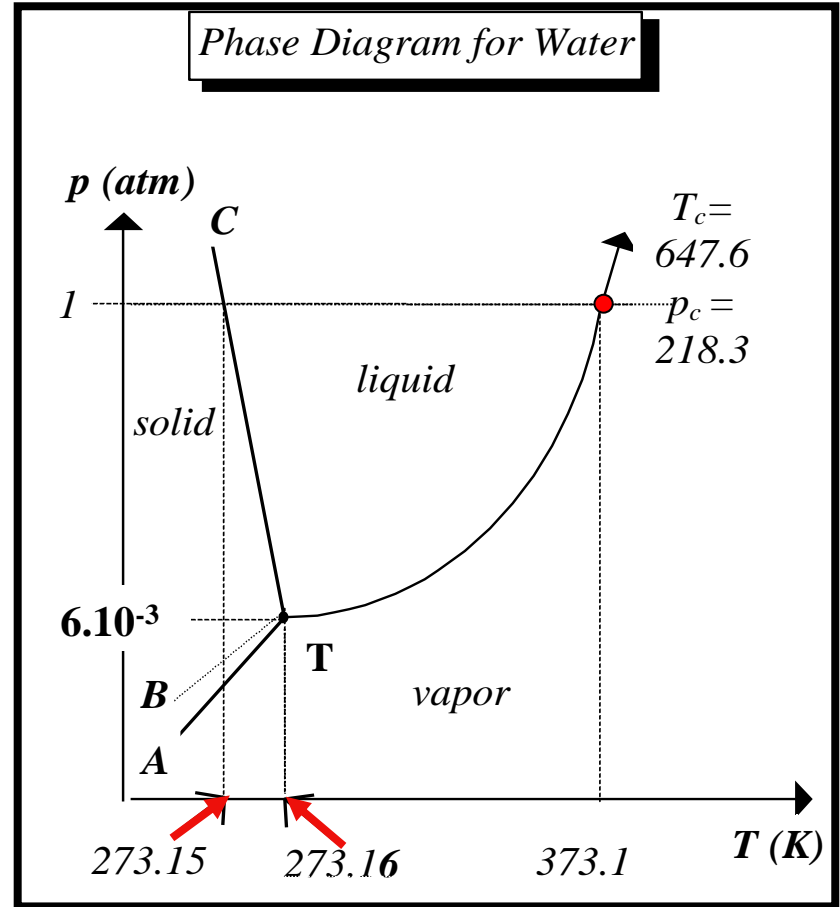
Artificial structure at low V: due to binning effects

Transitions of Phase

Large V , high T : vdW gas \rightarrow ideal gas
 small V , low T : vdW gas \rightarrow real gas



Shaded: negative pressures, substance does not exist as gas, liquefaction, liquid-gas coexistence, freezing to solid.



Material	Formula	Critical pressure P_c		Critical temperature T_c		$k = C_p/C_v$
		psia	bar (abs)	$^{\circ}\text{F}$	$^{\circ}\text{C}$	
Water	H_2O	3206	221	705	374	1.32

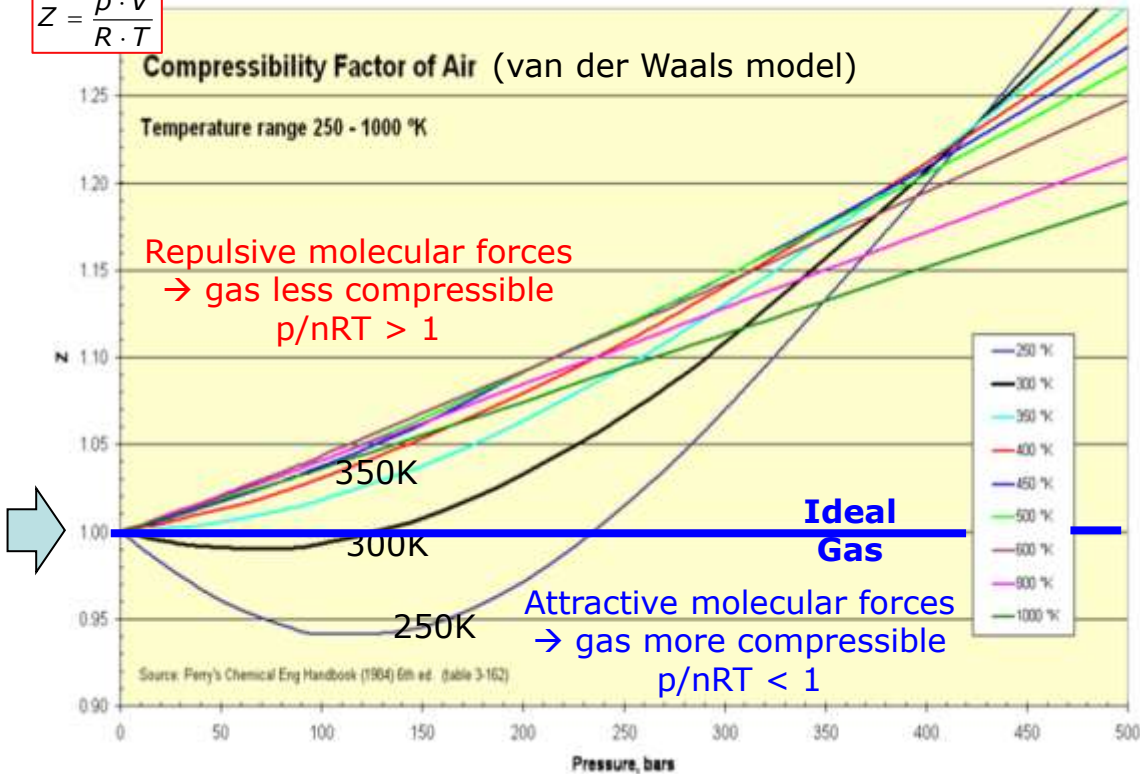
Compression Factor: Virial Expansions

Virial expansion of compression factor:
$$Z = \frac{p \cdot V}{R \cdot T} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots =: \sum_{n=0}^{\infty} \frac{c_n(T)}{V^n}$$

Volume of real gas @ p:
$$V = Z \cdot (p^{-1} \cdot R \cdot T)$$

Alternative expansion:
$$Z = \frac{p \cdot V}{R \cdot T} = 1 + B'(T)p + C'(T)p^2 + \dots =: \sum_{n=0}^{\infty} c'_n(T)p^n$$

$$Z = \frac{p \cdot V}{R \cdot T}$$



Related:

Isothermal compressibility

$$\kappa_T := -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Volume expansion coefficient

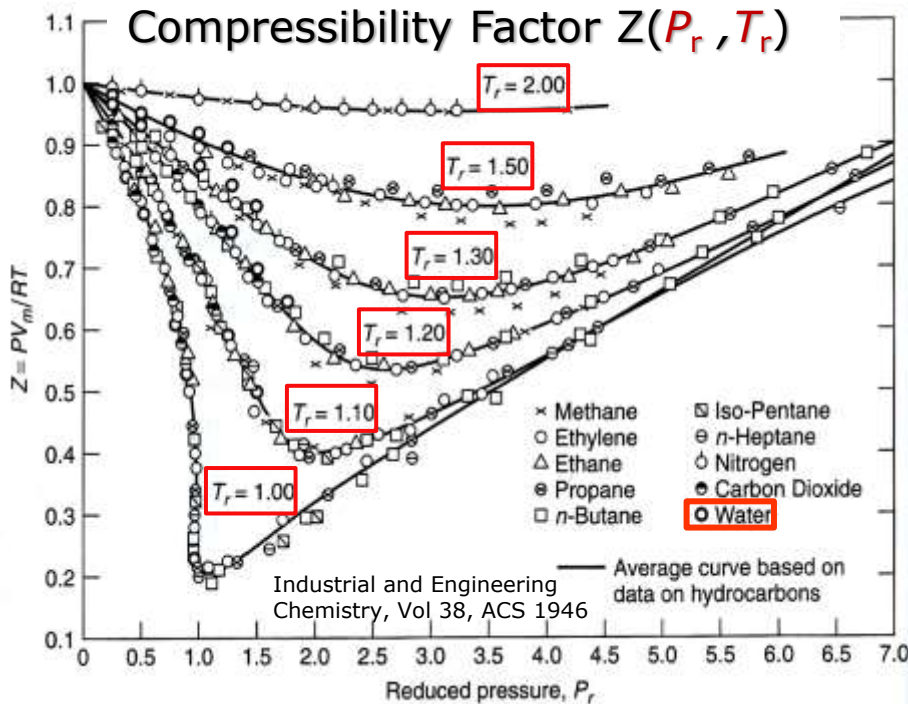
$$\alpha := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

Heat capacities

$$C_p - C_v = \frac{\alpha^2}{\kappa_T} \cdot V \cdot T$$

Phenomen 1&2. LTD

Law of Corresponding States

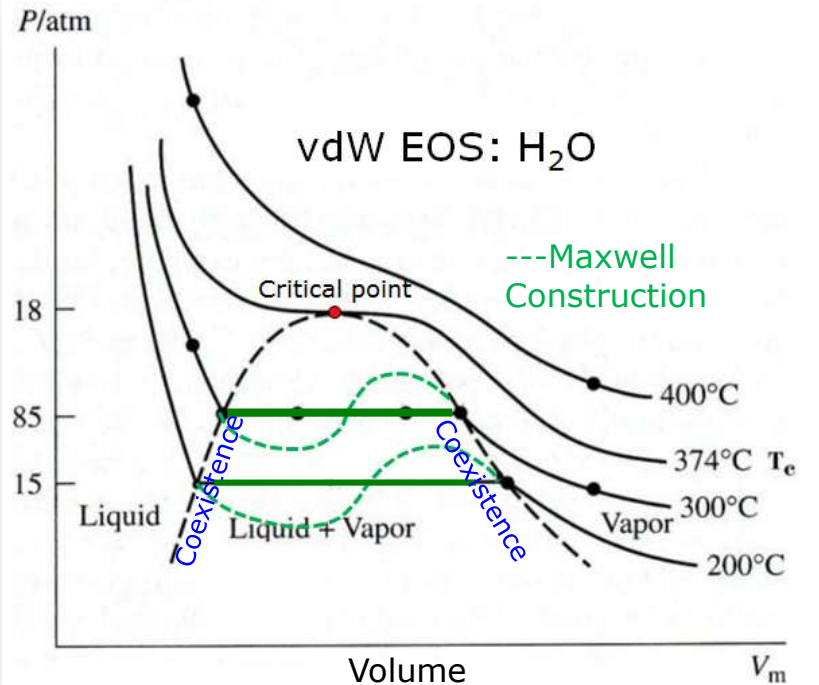


Law of Corresponding States

According to van der Waals, any gas :

$$\left(p_r + \frac{3}{V_r^2}\right) \cdot (3V_r - 1) = 8 \cdot T_r$$

dp/dV instability \rightarrow condensation
 \rightarrow Coexistence of phases



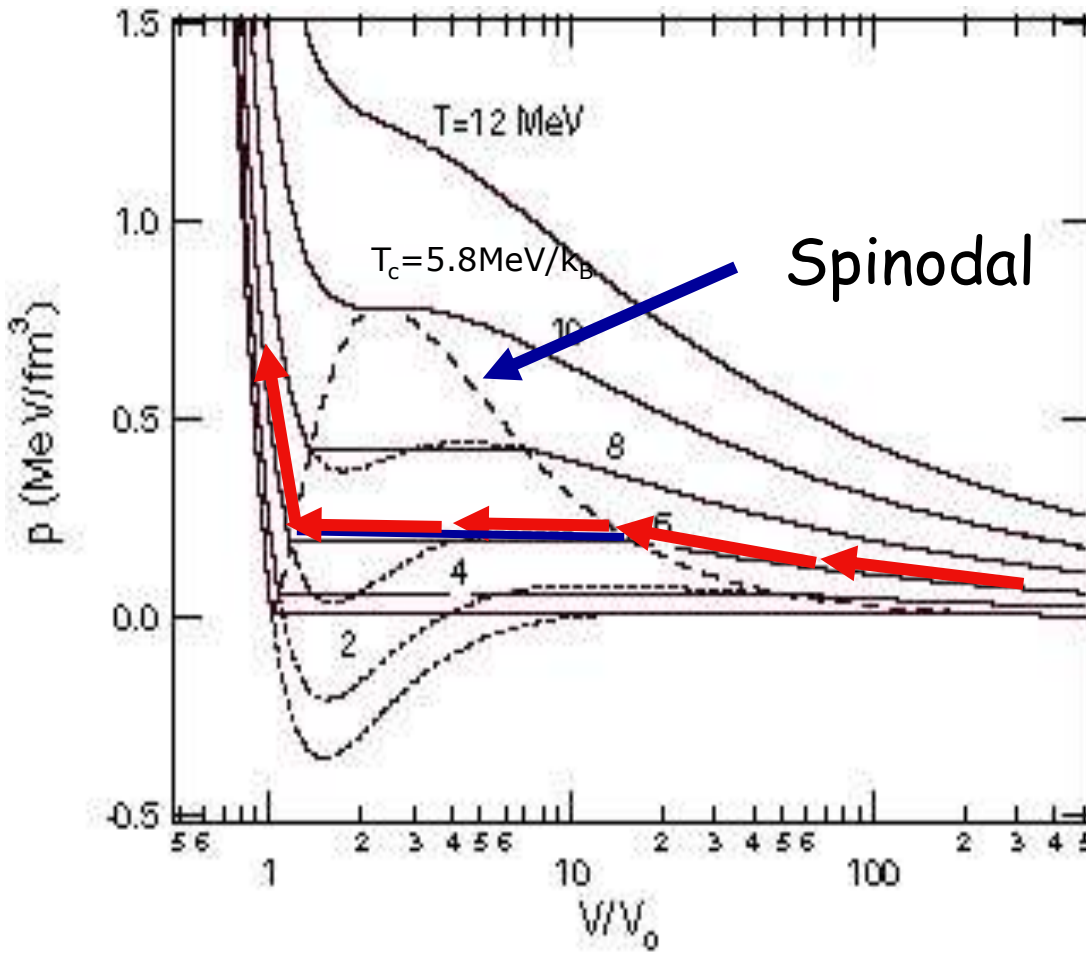
$$\left(p + \frac{n^2 \cdot a}{V^2}\right) \cdot (V - n \cdot b) = n \cdot R \cdot T$$

Critical Point $\left(\frac{\partial p}{\partial V}\right)_{T=\text{const}} = 0 = \left(\frac{\partial^2 p}{\partial V^2}\right)_{T=\text{const}}$

$$\rightarrow p_c = \frac{a}{27b^2}, V_c = 3nb, T_c = \frac{8a}{27bR}$$

$p_r := p/p_c, V := V/V_c, T_r := T/T_c$
 \rightarrow reduced EOS for all vdW gases

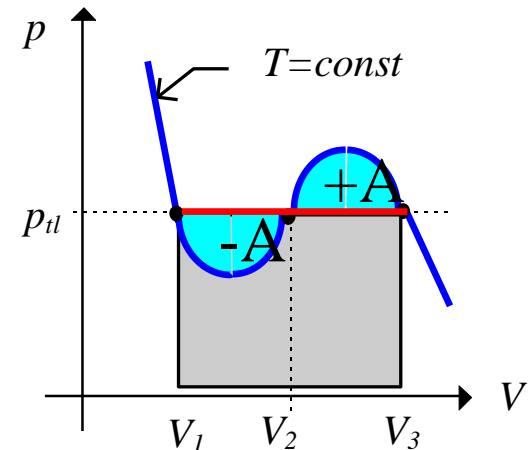
Real Gas of Nucleons



Compression leads to liquefaction.

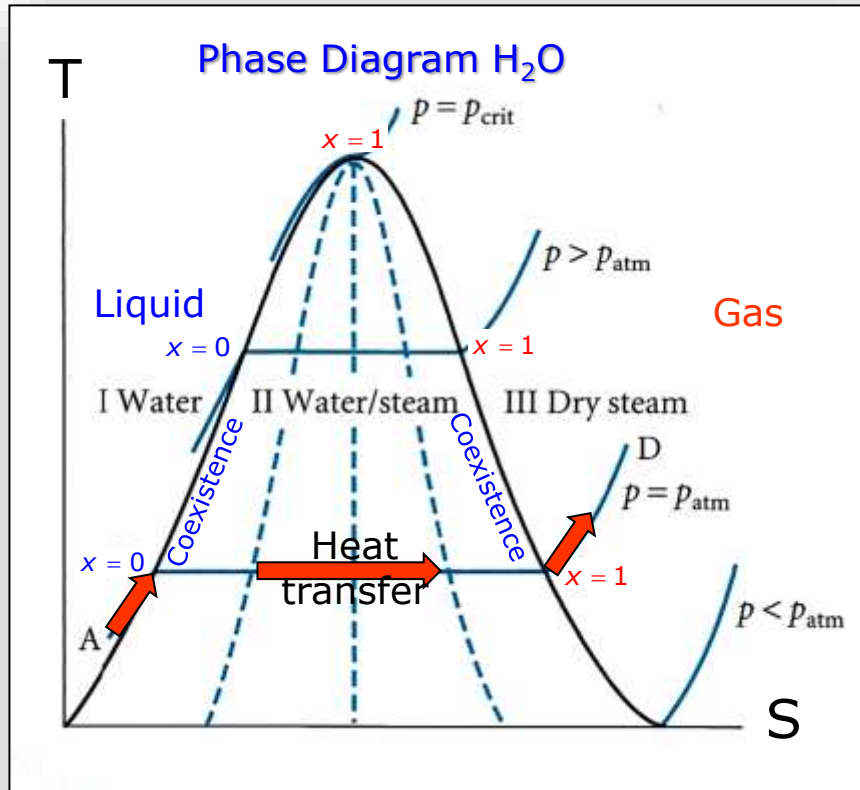
“Tie-line” pressure from Maxwell construction: $+A = |-A|$

Maxwell Construction



Steam: Driving Gas for TD Engines

After Andrews & Jelley



To use steam as driving gas for thermal engines, energy has to be transferred to water at T_l (e.g., 25°C)

- 1) to heat it to (100°C)
- 2) to evaporate H_2O (@ 100°C),
- 3) to heat the vapor $100^\circ\text{C} \rightarrow T_h$

$$p = 1 \text{ atm (bar)} = 101.33 \text{ kN/m}^2$$

\rightarrow Water boils @ at 100°C

\rightarrow Need $419 \text{ kJ/kg H}_2\text{O}$ to heat water from 0°C to $T = 100^\circ\text{C}$.

\rightarrow @ 101.33 kN/m^2 and 100°C

Specific enthalpy H_2O :

$$h_{\text{water}}(100^\circ\text{C}) = 419 \text{ kJ/kg.}$$

Specific enthalpy of evaporation:

$$h_{\text{evap}}(100^\circ\text{C}) = 2,257 \text{ kJ/kg}$$

(not needed for ideal gas):

Total heat required at $p = \text{const.}$ to convert H_2O to steam @ 100°C :

$$h_{\text{steam}}(100^\circ\text{C}) = (419 + 2,257) \text{ kJ/kg} = 2,676 \text{ kJ/kg} = 2.676 \text{ (MJ/kg)} = 0.74 \text{ kWh/kg}$$

$$\text{L-G mixture} \quad h_s(x) = (1-x) \cdot h_{\text{water}} + x \cdot h_{\text{steam}} \quad \text{Extensive}$$

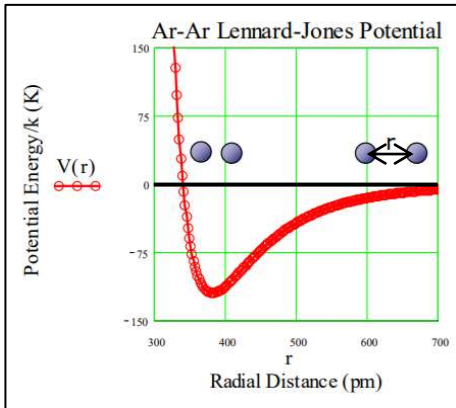
$$\text{Similar:} \quad u_s(x) = (1-x) \cdot u_{\text{water}} + x \cdot u_{\text{steam}} \quad \text{Quantities (U, H, S,...)}$$

Critical TD Parameters for Real Gases

Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Acetic Acid	CH3-CO-OH	841	58	612	322	1.15
Acetone	CH3-CO-CH3	691	47.6	455	235	-
Acetylene	C2H2	911	62.9	97	36	1.26
Air	O2+N2	547	37.8	-222	-141	1.4
Ammonia	NH3	1638	113	270	132	1.33
Argon	A	705	48.6	-188	-122	1.67
Benzene	C6H6	701	48.4	552	289	1.12
Butane	C4H10	529	36.5	307	153	1.09
Carbon Dioxide	CO2	1072	74	88	31	1.3
Carbon Monoxide	CO	514	35.5	-218	-139	1.4
Carbon Tetrachloride	CCl4	661	45.6	541	283	-
Chlorine	Cl2	1118	77	291	144	1.26
Ethane	C2H6	717	49.5	90		
Ethyl Alcohol	C2H5OH	927	64	469		
Ethylene	CH2=CH2	742	51.2	50		
Ethyl Ether	C2H5-O-C2H5	522	36	383		
Fluorine	F2	367	25.3	-247		
Helium	He	33.2	2.29	-450		
Heptane	C7H16	394	27.2	513		
Hydrogen	H2	188	13	-400		
Hydrogen Chloride	HCl	1199	82.6	124		

Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Isobutane	(CH3)CH-CH3	544	37.5	273	134	1.1
Isopropyl Alcohol	CH3-CHOH-CH3	779	53.7	455	235	-
Methane	CH4	673	46.4	-117	-83	1.31
Methyl Alcohol	H-CH2OH	1156	79.6	464	240	1.2
Nitrogen	N2	492	34	-233	-147	1.4
Nitrous Oxide	N2O	1054	72.7	99	37	1.3
Octane	CH3-(CH2)6- CH3	362	25	565	296	1.05
Oxygen	O2	730	50.4	-182	-119	1.4
Pentane	C5H12	485	33.5	387	197	1.07
Phenol	C6H5OH	889	61.3	786	419	-
Phosgene	COCl2	823	56.7	360	182	-
Propane	C3H8	617	42.6	207	97	1.13
Propylene	CH2=CH-CH3	661	45.6	198	92	1.15
Refrigerant 12	CCl2F2	582	40.1	234	112	1.14
Refrigerant 22	CHClF2	713	49.2	207	97	1.18
Sulfur Dioxide	SO2	1142	78.8	315	157	1.29
Water	H2O	3206	221	705	374	1.32

Internal Energy of Real Gases



Effect of interaction on internal energy $U_{RG}(n, V, T)$.

What to expect?

Evaluate: use knowledge $U(n, V, T) \xrightarrow{V \rightarrow \infty} U_{IG}(n, V, T)$

$$U(n, V, T) = U_{IG}(n, V, T) - \int_V^{\infty} \left(\frac{\partial U}{\partial V} \right)_T dV \xrightarrow{V \rightarrow \infty} U_{IG}(n, V, T)$$



Express in terms of
EoS $\rightarrow \{V, p, T\}$



Helmholtz Eq.

$$\left(\frac{\partial U}{\partial V} \right)_T = T^2 \left(\frac{\partial p}{\partial V T} \right)_V$$

See later and
Kondepudi, Ch.5



$$U(n, V, T) = U_{IG}(n, V, T) - \int_V^{\infty} T^2 \left(\frac{\partial p}{\partial V T} \right)_V dV$$



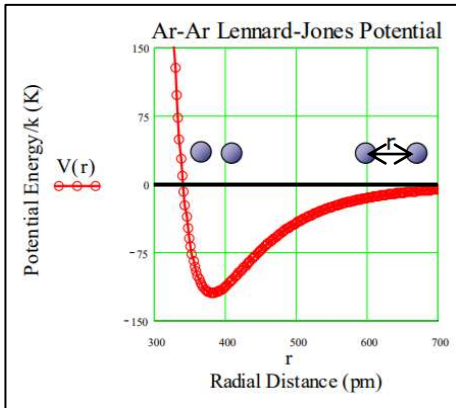
Generic
real-gas EoS

van der Waals
EoS

$$\frac{p}{T} = \frac{n \cdot R}{(V - n \cdot b)} - \frac{n^2 \cdot a}{T \cdot V^2} \rightarrow$$

$$T^2 \left(\frac{\partial p}{\partial V T} \right)_V = a \cdot \left(\frac{n}{V} \right)^2$$

Internal Energy of Real Gases



Effect of interaction on internal energy $U_{RG}(n, V, T)$.

Use knowledge $U(n, V, T) \xrightarrow{V \rightarrow \infty} U_{IG}(n, V, T)$

van der Waals EoS (**linear** function of **T**)

$$p = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2} \rightarrow T^2 \left(\frac{\partial p}{\partial V} \right)_V = a \cdot \left(\frac{n}{V} \right)^2$$

$$U(n, V, T) = U_{IG}(n, V, T) - a \cdot \left(\frac{n}{V} \right)^2 \cdot V < \underline{U_{IG}(n, V, T)}$$

Heat Capacity

$$C_V = C_{V,IG} - \frac{\partial}{\partial T} \int_V^\infty T^2 \left(\frac{\partial p}{\partial V} \right)_V dV$$

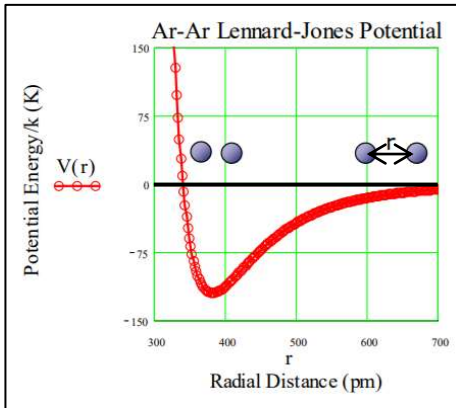
$$C_V = C_{V,IG} - \int_V^\infty T \left(\frac{\partial^2 p}{\partial T^2} \right)_V dV$$

➔ **vdW EoS**: $\partial^2 p / \partial T^2 = 0 \rightarrow$

$$C_V^{vdW} = C_{V,IG}$$

$$vdW \text{ EoS} \rightarrow C_p - C_V = \left(\alpha^2 / \kappa_T \right) \cdot V \cdot T$$

Free Energy of Real Gases: V and p Dependence



Use asymptotic equivalence of real and ideal gases, e.g.,

$$A(n, V, T) \xrightarrow{V \rightarrow \infty} A_{IG}(n, V, T)$$

$$\text{and } \left(\frac{\partial A}{\partial V} \right)_T = -p$$

Generic real-gas EoS

$$A(n, V, T) = A_{IG}(n, V, T) + \int_V^{\infty} (p - p_{IG}) dV \xrightarrow{V \rightarrow \infty} A_{IG}(n, V, T)$$

$$G(n, p, T) = G_{IG}(n, p, T) + \int_0^p (V - V_{IG}) dp \xrightarrow{p \rightarrow 0} G_{IG}(n, p, T)$$

Helmholtz free energy

$$A(n, V, T) = U - T \cdot S$$

Gibbs free energy

$$G(n, p, T) = H - T \cdot S$$

$$\text{Insert van der Waals Eos: } p_{vdW} = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2}$$

$$p_{vdW} - p_{IG} = n \cdot R \cdot T \left(\frac{(n \cdot b)}{V(V - n \cdot b)} \right) - \frac{n^2 \cdot a}{V^2}$$

*n moles/
particles*

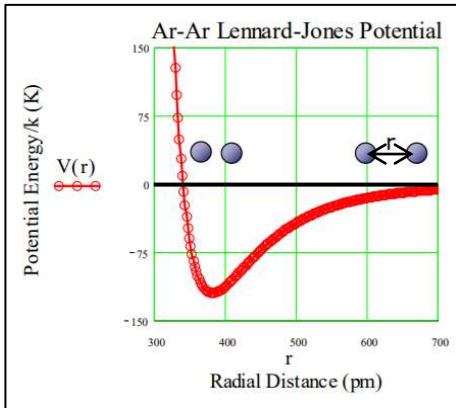
van der Waals EoS

$$A_{vdW}(n, V, T) = A_{IG}(n, V, T) - a \left(\frac{n}{V} \right)^2 - n \cdot R \cdot T \cdot \ln \left(1 - \frac{n \cdot b}{V} \right)$$

solve **A** for **S**

$$S_{vdW} = \frac{1}{T} \cdot (A_{vdW} - U_{vdW}) = n \cdot \left[s_0 + C_V \cdot \ln T + R \cdot \ln \left(\frac{(V - n \cdot b)}{n} \right) \right]$$

Chemical Potential of Real Gases: p Dependence



Use asymptotic equivalence of real and ideal gases,
 $G(p, T) \rightarrow$

$$\mu(p, T) = \mu_{IG}(p, T) + \int_0^p (V - V_{IG}) dp'$$

One mol: $V = Z \cdot R \cdot T \cdot p^{-1} \rightarrow \mu(p, T) = \mu_{IG}(p, T) + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p'} dp'$

$$\mu(p, T) = \left[\mu_{IG}(p_0, T) + R \cdot T \cdot \ln\left(\frac{p_{IG}}{p_0}\right) \right] + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p'} dp' \quad \leftarrow = f(n, a, b)$$

Chemical potential

$$\mu(p, T) = \left(\frac{\partial G(p, T)}{\partial n} \right)_{p, T}$$

Pressure equivalent "Fugacity" f : $\ln\left(\frac{f}{p}\right) := \int_0^p \frac{(Z-1)}{p'} dp'$; $\lim_{p \rightarrow 0} (f/p) = 1$
 "Activity" $a := f/p$

$$\ln\left(\frac{f}{p}\right) \approx B'(T) \cdot p + \frac{1}{2} C'(T) \cdot p^2 + \dots \rightarrow \text{Virial expansion of real-gas EoS}$$

Virial coefficients B' and C' from fit of Z to EoS.
 Found in tables or can be calculated from EoS parameters.

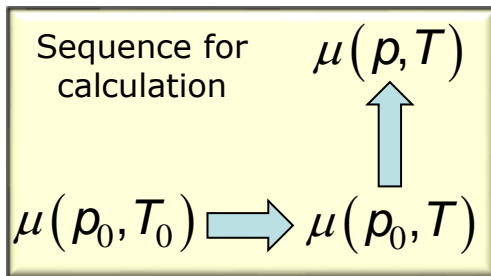
$$\mu(p, T) \approx \mu_{IG}(p_0, T) + R \cdot T \cdot \left[B'(T) \cdot p + \frac{1}{2} C'(T) \cdot p^2 \right]$$

Chemical Potential of Real Gases: T Dependence

Calculate chemical potential of real gases from relations to ideal gases @ p_0, T_0

$$\mu(p, T) = \left[\mu_{IG}(p_0, T) + R \cdot T \cdot \ln\left(\frac{p_{IG}}{p_0}\right) \right] + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p} dp$$

➔ Tabulations are normally as Gibbs energies of formation $\Delta G_f^0 = \mu(p_0, T_0)$
 @ $p_0 = 1\text{bar}, T_0 = 298.15\text{K}$ → need to scale up. Since $\mu \rightarrow \mathbf{G(p, T)}$:



Per mol $G(p, T) = H - T \cdot S = H + T \cdot \left(\frac{\partial G}{\partial T} \right)_p$

$$\rightarrow -\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p = -\frac{H}{T^2}$$

Gibbs-Helmholtz Equation

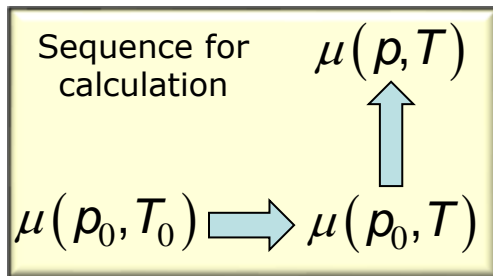
$$\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2}$$

Parameterizing the Chemical Potential

Calculate chemical potential of real gases from relations to ideal gases @ p_0

$$\mu(p, T) = \left[\mu_{IG}(p_0, T) + R \cdot T \cdot \ln\left(\frac{p_{IG}}{p_0}\right) \right] + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p} dp \quad \frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2}$$

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$$\mu(p_0, T) = \frac{T}{T_0} \mu(p_0, T_0) - T \cdot \int_{T_0}^T \frac{H(p_0, T')}{T'^2} dT'$$

$$\mu(p, T) = \mu(p_0, T) + \int_{p_0}^p V(p', T) dp'$$

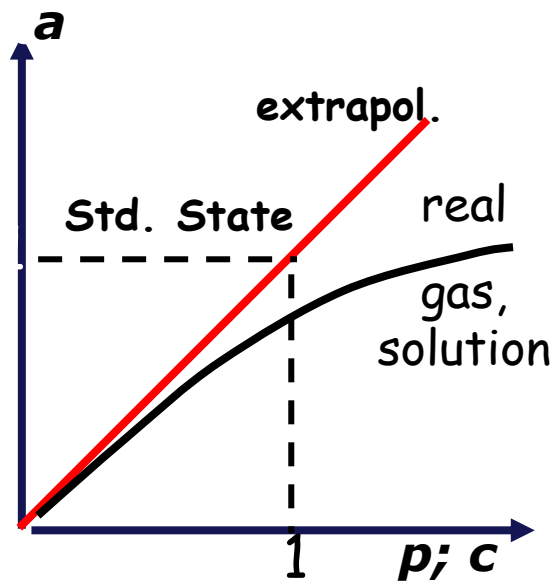
$$H(p, T) = \int_0^T C_p(T') dT'$$

Molar heat capacity $C_p(T) = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^{-2}$

Gas	A (J mol ⁻¹ K ⁻¹)	B (10 ⁻³ J mol ⁻¹ K ⁻²)	C (10 ⁻⁶ J mol ⁻¹ K ⁻³)	D (10 ⁻⁹ J mol ⁻¹ K ⁻⁴)	E (10 ⁶ J mol ⁻¹ K ⁻⁵)
O ₂ (g)	29.66	6.137	-1.186	0.0958	-0.2197
N ₂ (g)	29.09	8.218	-1.976	0.1592	0.0444
CO ₂ (g)	24.99	55.19	-33.69	7.948	-0.1366

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Effective Pressures of Liquids and Solids



Non-ideal behavior of gases (at high pressures) and of solutions.

Effective quantities simulating pressure of an ideal gas and all the associated laws.

$$\text{Activity } a: G(a) = G^\circ + nRT \cdot \ln(a)$$

$$G^\circ = G(\text{standard state}) \quad 1M$$

$$\text{ideal gas } a = p / 1\text{atm}$$

$$\text{real gas } a = \gamma \cdot p \quad \gamma = \text{activity coefficient}$$

$$\text{pure solids or liquids } a = 1$$

$$\text{solutions } a = \gamma \cdot c \quad c = \text{concentration (mol / L)}$$

$$\text{standard state: } \gamma = 1 \text{ like dilute solutions}$$

$$\text{solvent: } a = \gamma \cdot x \quad x = \text{mole fraction}$$

$$\text{Real gas } a = \frac{f}{p} \rightarrow \text{"Fugacity" } f: \quad \ln\left(\frac{f}{p}\right) = \int_0^p \frac{(Z-1)}{p} dp;$$

$$\text{Pure solids and liquids: } a_k \approx 1$$

$$\text{Solutions with mole fraction } x_k \text{ and activity coefficient } \gamma_k: \quad a_k \approx \gamma_k \cdot x_k$$

Gibbs Energy in Chemical Reactions

Generic reaction $A + B \rightarrow C + D$ in equilibrium $\rightarrow \mu_C + \mu_D - \mu_A - \mu_B = 0$

$$\mu_k(p, T) = \mu_k^0(T) + R \cdot T \cdot \ln(a_k) \rightarrow a_k = \exp \left\{ \frac{\mu_k(p, T) - \mu_k^0(T)}{R \cdot T} \right\}$$

Standard molar Gibbs energy of formation $\mu_k^0(T) = \Delta G_f^0(k, T)$

Equilibrium
Constant (T)

$$K(T) = \frac{a_C \cdot a_D}{a_A \cdot a_B} = \exp \left\{ - \frac{\mu_C^0 + \mu_D^0 - \mu_A^0 - \mu_B^0}{R \cdot T} \right\}$$

Meaning of activity a_k : nominally replaces pressure in TD relations

Ideal gas, partial pressure p_k : $a = \frac{p_k}{p_0}$;

Real gas $a = \frac{f}{p} \rightarrow$ "Fugacity" f : $\ln\left(\frac{f}{p}\right) = \int_0^p \frac{(Z-1)}{p} dp$;

Pure solids and liquids: $a_k \approx 1$

Solutions with mole fraction x_k and activity coefficient γ_k : $a_k \approx \gamma_k \cdot x_k$

Critical TD Parameters for Real Gases

Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Acetic Acid	CH3-CO-OH	841	58	612	322	1.15
Acetone	CH3-CO-CH3	691	47.6	455	235	-
Acetylene	C2H2	911	62.9	97	36	1.26
Air	O2+N2	547	37.8	-222	-141	1.4
Ammonia	NH3	1638	113	270	132	1.33
Argon	A	705	48.6	-188	-122	1.67
Benzene	C6H6	701	48.4	552	289	1.12
Butane	C4H10	529	36.5	307	153	1.09
Carbon Dioxide	CO2	1072	74	88	31	1.3
Carbon Monoxide	CO	514	35.5	-218	-139	1.4
Carbon Tetrachloride	CCl4	661	45.6	541	283	-
Chlorine	Cl2	1118	77	291	144	1.26
Ethane	C2H6	717	49.5	90		
Ethyl Alcohol	C2H5OH	927	64	469		
Ethylene	CH2=CH2	742	51.2	50		
Ethyl Ether	C2H5-O-C2H5	522	36	383		
Fluorine	F2	367	25.3	-247		
Helium	He	33.2	2.29	-450		
Heptane	C7H16	394	27.2	513		
Hydrogen	H2	188	13	-400		
Hydrogen Chloride	HCl	1199	82.6	124		

Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Isobutane	(CH3)CH-CH3	544	37.5	273	134	1.1
Isopropyl Alcohol	CH3-CHOH-CH3	779	53.7	455	235	-
Methane	CH4	673	46.4	-117	-83	1.31
Methyl Alcohol	H-CH2OH	1156	79.6	464	240	1.2
Nitrogen	N2	492	34	-233	-147	1.4
Nitrous Oxide	N2O	1054	72.7	99	37	1.3
Octane	CH3-(CH2)6-CH3	362	25	565	296	1.05
Oxygen	O2	730	50.4	-182	-119	1.4
Pentane	C5H12	485	33.5	387	197	1.07
Phenol	C6H5OH	889	61.3	786	419	-
Phosgene	COCl2	823	56.7	360	182	-
Propane	C3H8	617	42.6	207	97	1.13
Propylene	CH2=CH-CH3	661	45.6	198	92	1.15
Refrigerant 12	CCl2F2	582	40.1	234	112	1.14
Refrigerant 22	CHClF2	713	49.2	207	97	1.18
Sulfur Dioxide	SO2	1142	78.8	315	157	1.29
Water	H2O	3206	221	705	374	1.32