Thermodynamics: Phenomenology

- Work and other forms of energy

    Transfer and dissipation

    - 1. & 2. Fundamental Laws of Thermodynamics

- Ideal-gas laws and simple processes

    Technological applications, cyclic engines

- Real gases equation of state

    Technological applications

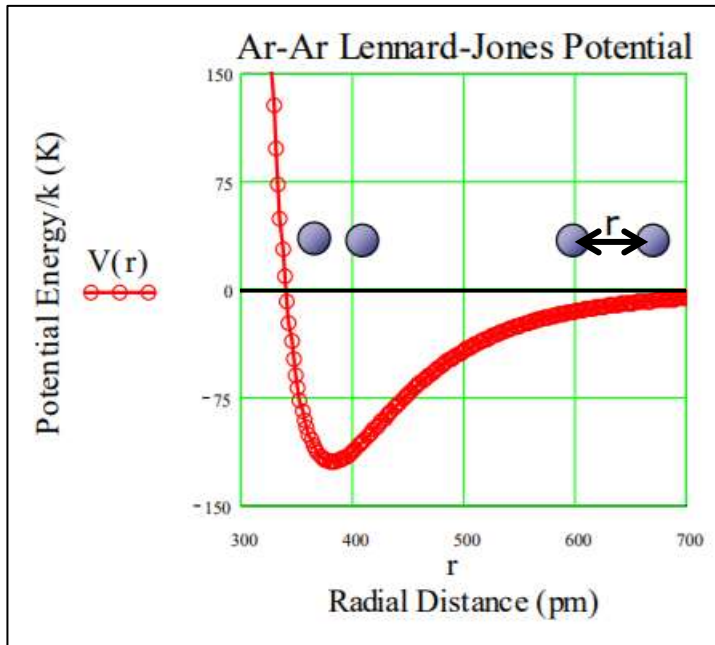- Phase equilibria

- Free energy in chemical reactions

1

Phen Real Gases

Real Substances

Ar-Ar Lennard-Jones Potential

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

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 > 5L/mol (diatomic), V > 20 L/mol (complex)

→ Real gas molecules interact with each other → motion is more or less free depending on density, pressure, temperature
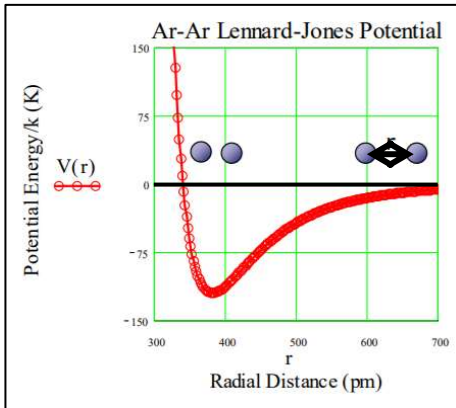
→ Different phases of substances:
Low density → gas
High densities (small distances) → liquid or solid behavior.

→ 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

Ar-Ar Lennard-Jones Potential

Potential Energy/k (K)

V(r)

Radial Distance (pm)

Excluded Volume

Hard-sphere interactions

2R

R

High densities = small distances) → excluded volume

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

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

Effective volume for N particles: $V \rightarrow V_{eff} = V - 8 \cdot N \cdot \upsilon$
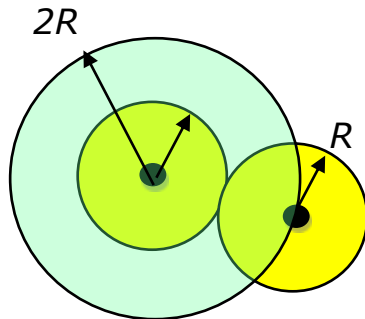
$$V_{eff} = V \cdot \left(1 - 8 \cdot \rho \cdot \upsilon\right) < V$$

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

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

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

Effective Pressure of Real Gases/ vdW EoS

Ar-Ar Lennard-Jones Potential
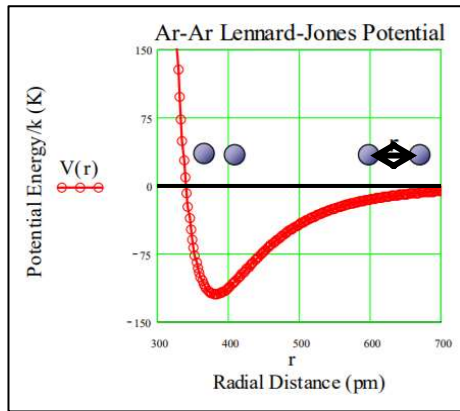
Without interaction: $<E>=(1/2)k_BT$ per *d.o.f.* $\rightarrow K=(3/2)k_BT$
*Long-range part of **L-J*** potential= attractive force, retards the
motion of the particles $\rightarrow K < (3/2)k_BT \rightarrow p_{real} < p_{IG}$

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

$$\rightarrow \Delta p \propto \rho^2 \rightarrow \Delta p \sim \rho^2 \approx -a \cdot \frac{N^2}{V^2} \text{ with } a > 0$$
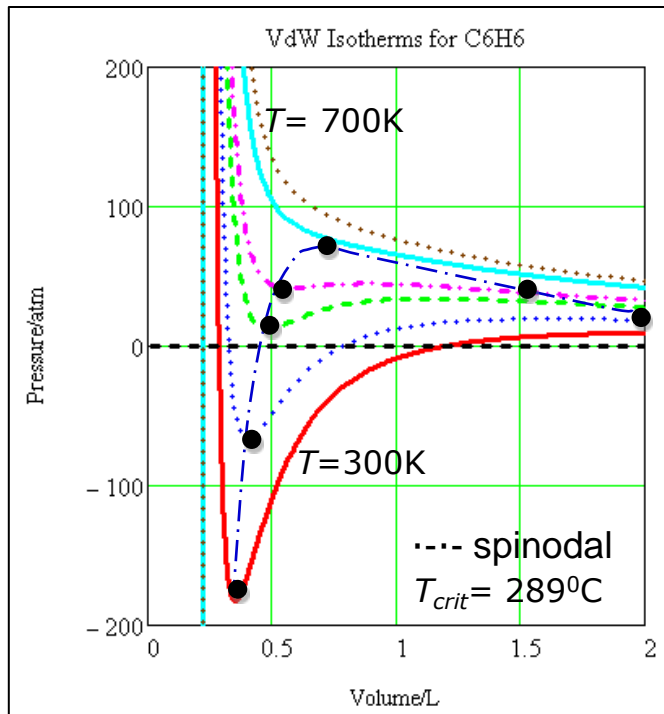
Observed pressure for real gas $p_{meas} < p_{IG}$.

$$p_{meas} = p_{IG} - \Delta p$$
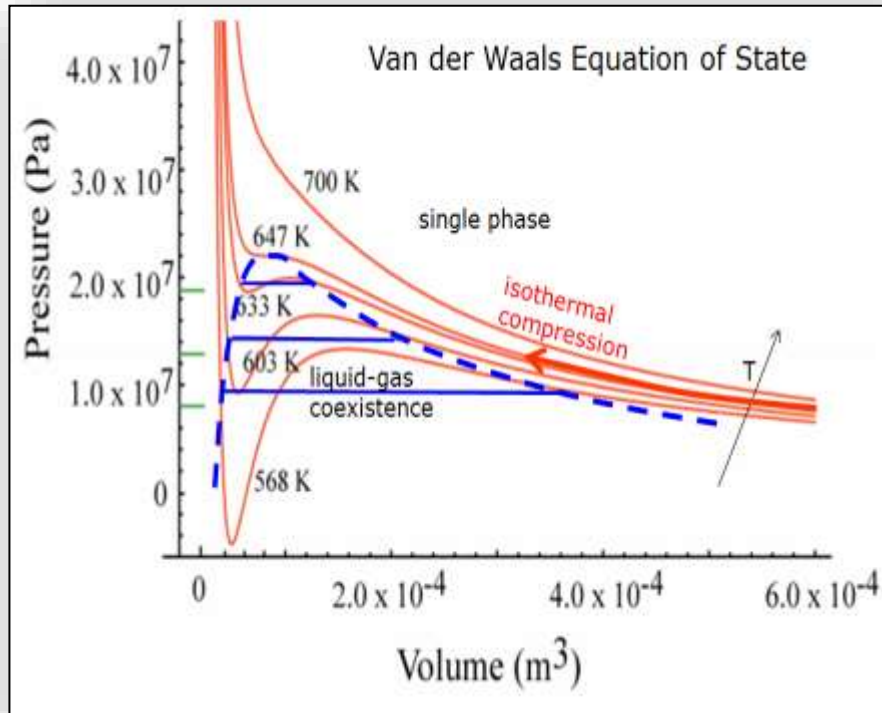$$Nk_BT = p_{IG} \cdot V_{eff} = (p_{meas} - \Delta p) \cdot V \cdot (1 - 8\rho\upsilon)$$

$$\boxed{\left(p + a\left(\frac{N}{V}\right)^2 \right) \cdot (V - Nb) = Nk_BT}$$

van der Waals EoS
for real gases

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

Phen Real Gases

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Parameterization of Real Gases

Ideal gas approximation good: V > 5L/mol (diatomic), V > 20 L/mol (complex)
Real-gas EoS non-monotonic → liquid-gas instability.

Corrections for inaccessible volume
and reduced pressure.

Expectations: High T, low ρ
→IG approximation good

High density: accessible volume
smaller than geometrical
container. Thermal-kinetic
motion changed by scattering.

Successful 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 :

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

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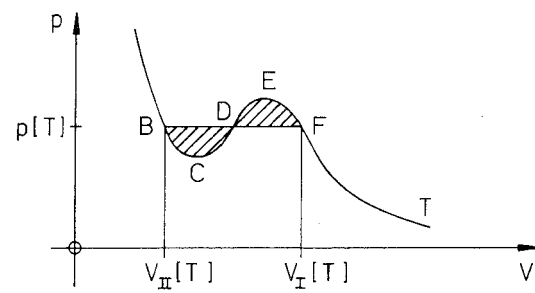
- Phase equilibria

- Free energy in chemical reactions

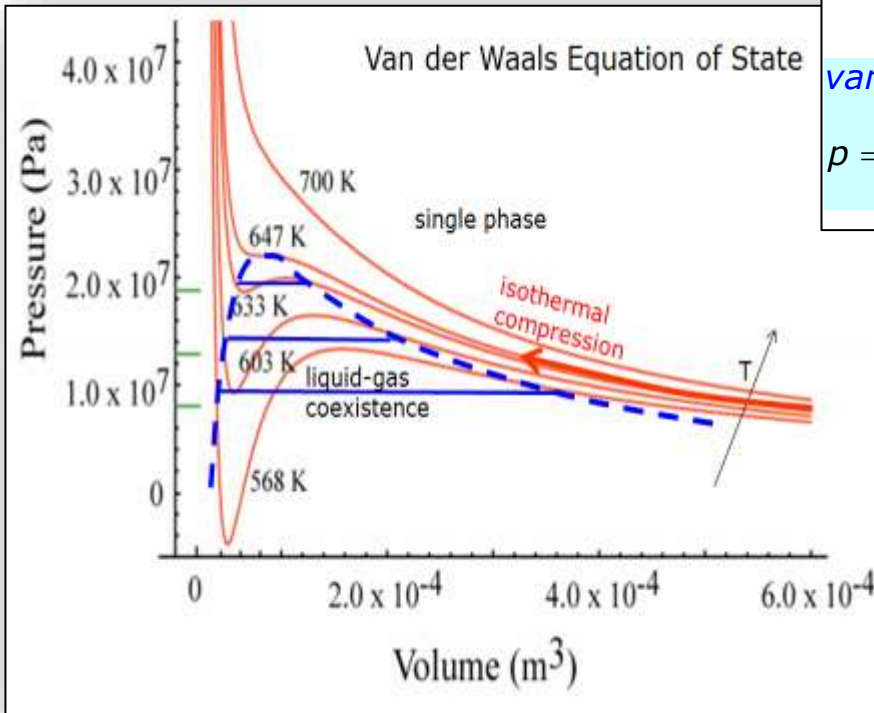**Reading Assignments**
Weeks 13&14
LN V-VI:

Kondepudi Ch. 6 & 7
Additional Material

McQuarrie & Simon
Ch. 7 & 8

Phen Real Gases

Parameterization of Real Gases

Ideal gas approximation good: V > 5L/mol (diatomic), V > 20 L/mol (complex)
Real-gas EoS non-monotonic → 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**) → liquifaction

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

Real-Gas Equation of State

van der Waals EOS H2O

van der Waals EOS C6H6
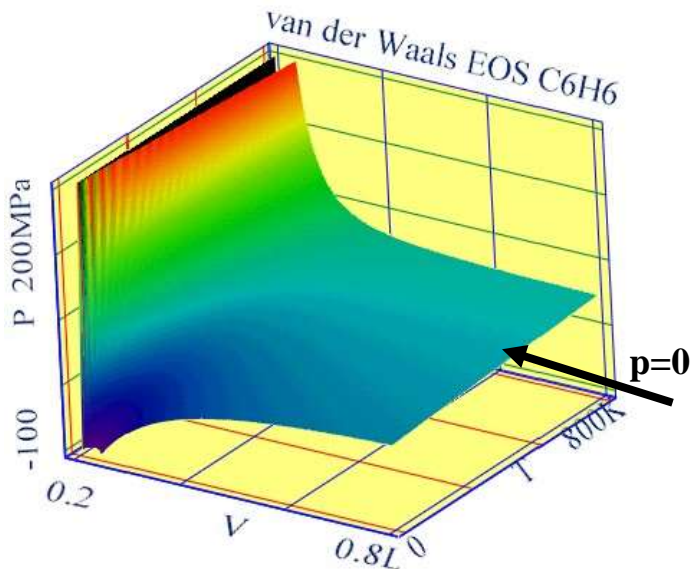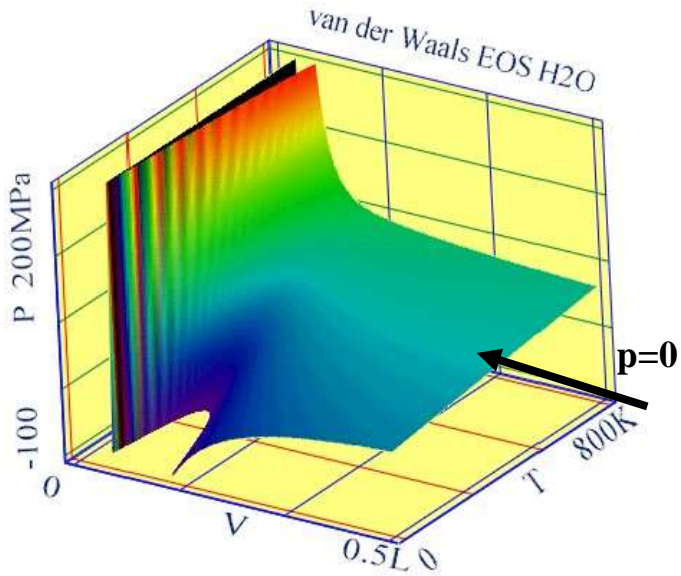
van der Waals: effects taken into account

a) average volume taken by gas particles → available volume reduced. → parameter **b**

b) collisions between particles reduce the actual pressure, attractive interactions.

   → $N_{coll} \propto$ (density)**²**,

   → scaling parameter **a**

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

Transitions of Phase

van der Waals EOS C6H6

$p < 0$

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

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

Phase Diagram for Water

p *(atm)*

C

1

$T_c = 647.6$

$p_c = 218.3$

liquid

solid

6.10^{-3}

T

B

vapor

A

273.15   273.16   373.1   *T (K)*
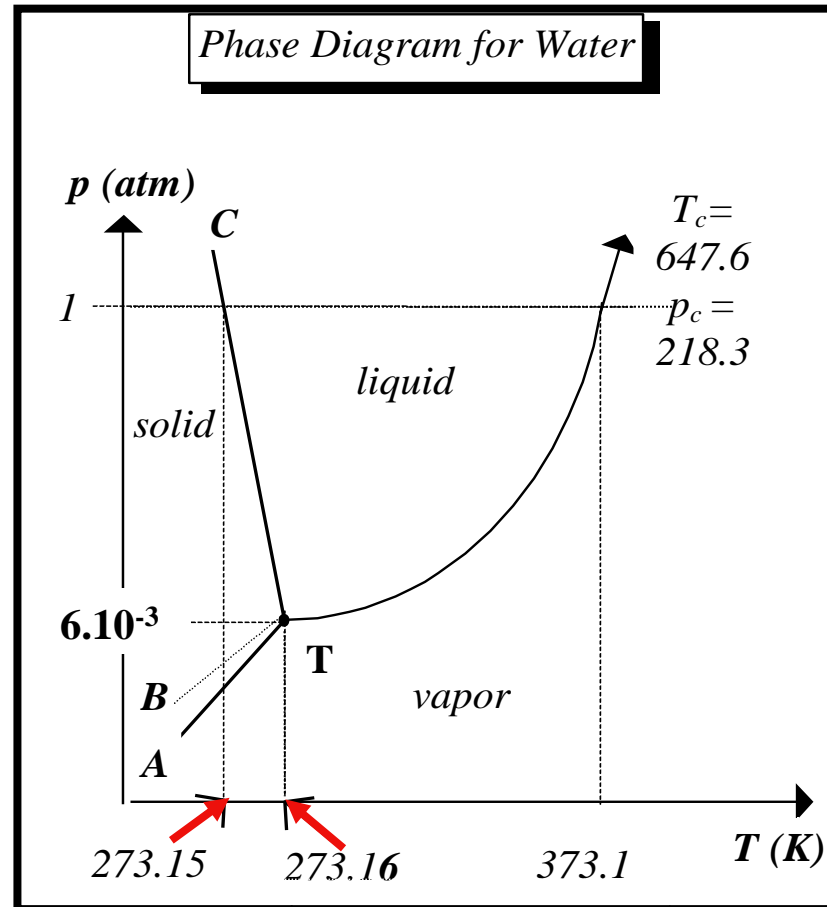
Generic Phase Diagram
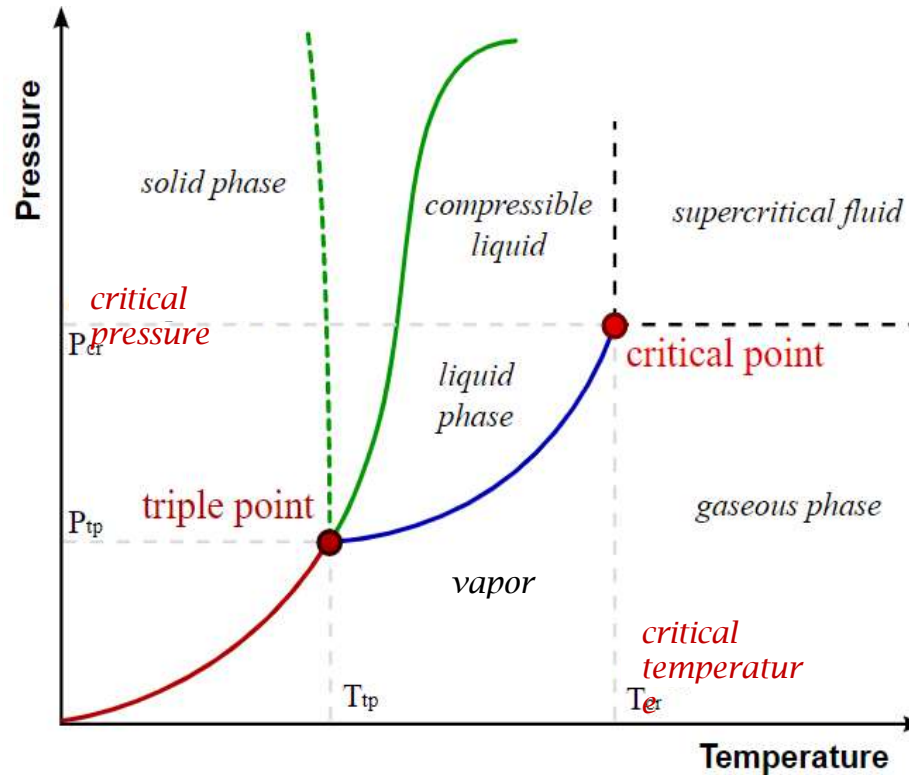
		Critical pressure P_c		Critical temperature T_c		
Material	Formula	psia	bar (abs)	°F	°C	$k = C_p/C_v$
Water	H_2O	3206	221	705	374	1.32

Compression Factor: Virial Expansions

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

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

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

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

Compressibility Factor of Air (van der Waals model)

Temperature range 250 - 1000 °K

Repulsive molecular forces
→ gas less compressible
p/nRT > 1

350K

300K

Ideal Gas

Attractive molecular forces
→ gas more compressible
p/nRT < 1

250K

Source: Perry's Chemical Eng Handbook (1984) 6th ed. (table 3-162)

Pressure, bars

Legend: —250 °K, —300 °K, —350 °K, —400 °K, —450 °K, —500 °K, —600 °K, —800 °K, —1000 °K
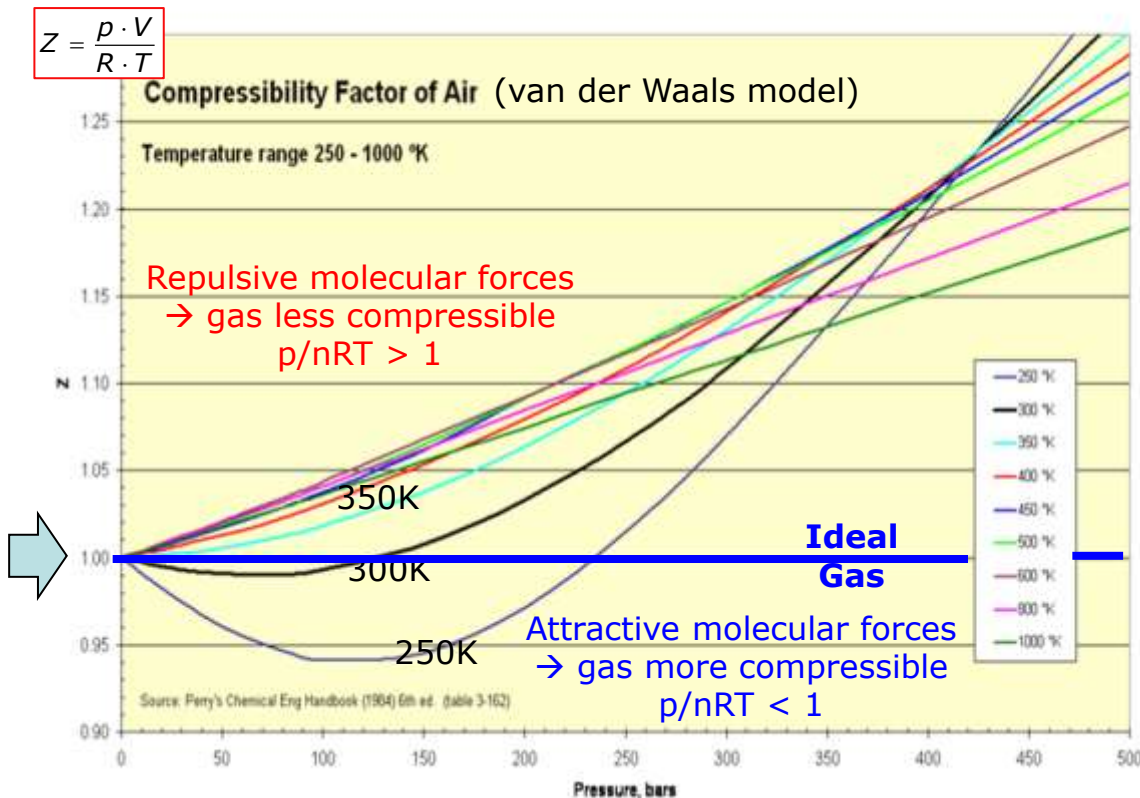
Related:

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

Law of Corresponding States
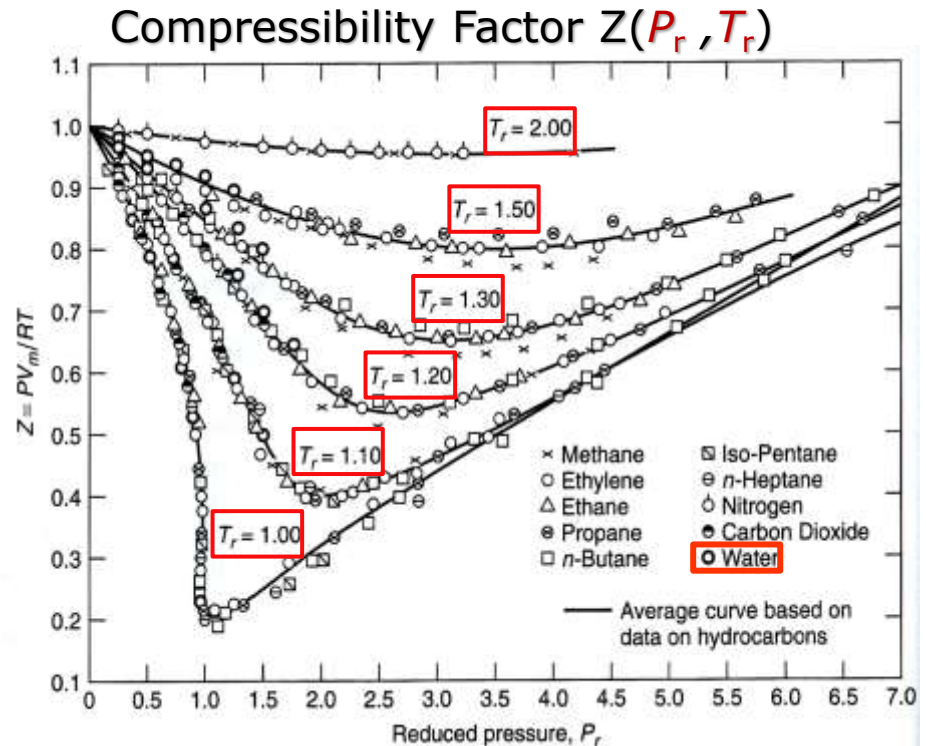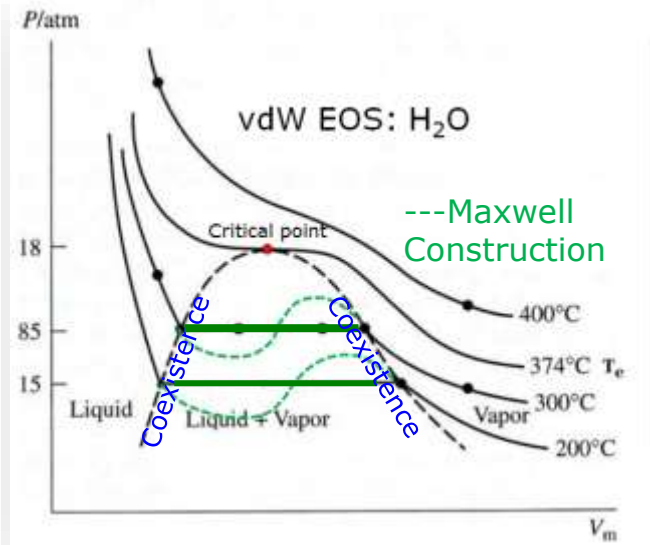
Compressibility Factor $Z(P_r, T_r)$

vdW EOS: H_2O

---Maxwell Construction

Coexistence

P/atm, Critical point, Liquid, Liquid + Vapor, Vapor, V_m, $400°C$, $374°C$ T_e, $300°C$, $200°C$

$Z = PV_m/RT$ vs Reduced pressure, P_r

$T_r = 2.00$, $T_r = 1.50$, $T_r = 1.30$, $T_r = 1.20$, $T_r = 1.10$, $T_r = 1.00$

× Methane ⊠ Iso-Pentane
○ Ethylene ⊖ n-Heptane
△ Ethane ◊ Nitrogen
⊖ Propane ⊙ Carbon Dioxide
□ n-Butane ○ Water

— Average curve based on data on hydrocarbons

Industrial and Engineering Chemistry, Vol 38, ACS 1946

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

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

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

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

Law of Corresponding States
According to van der Waals, any gas :

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

Real Gas of Nucleons

T=12 MeV

$T_c = 5.8 MeV/k_B$

Spinodal

p (MeV/fm^3)

V/V_o
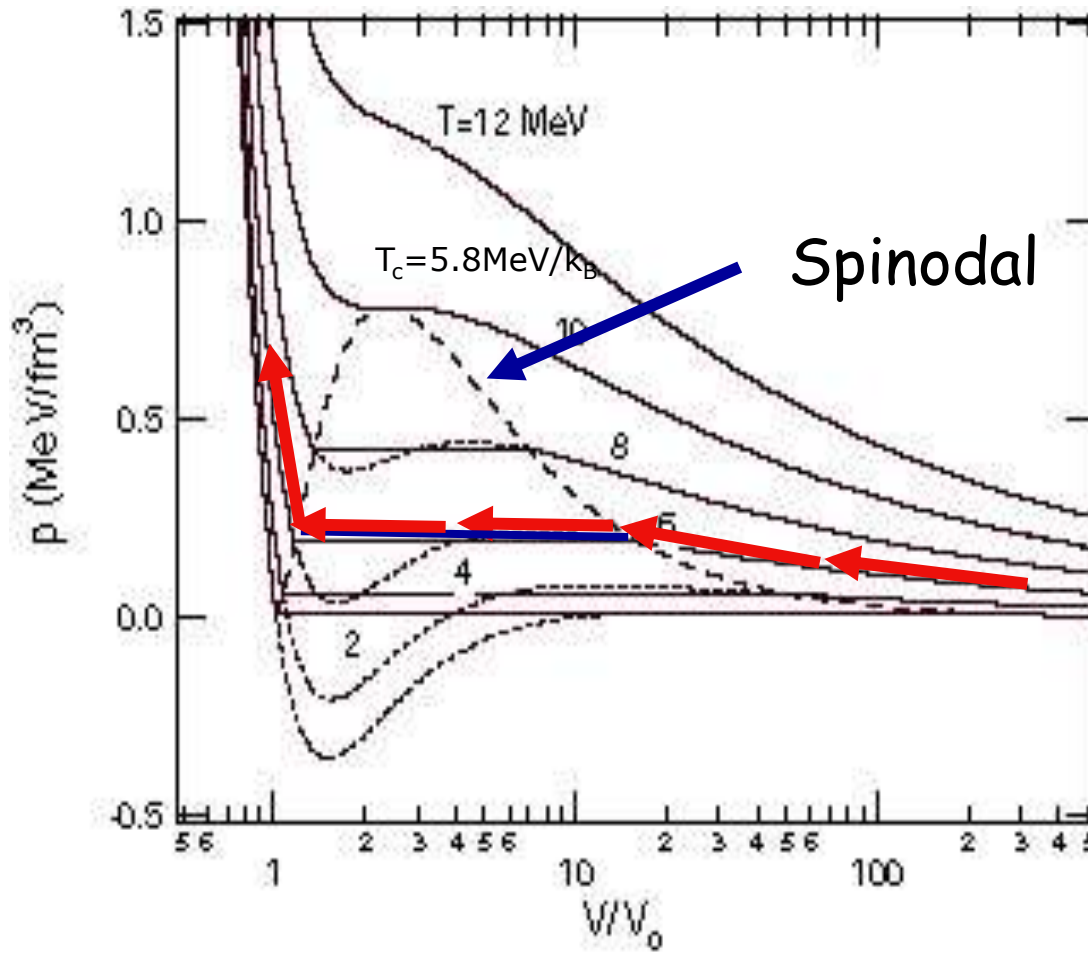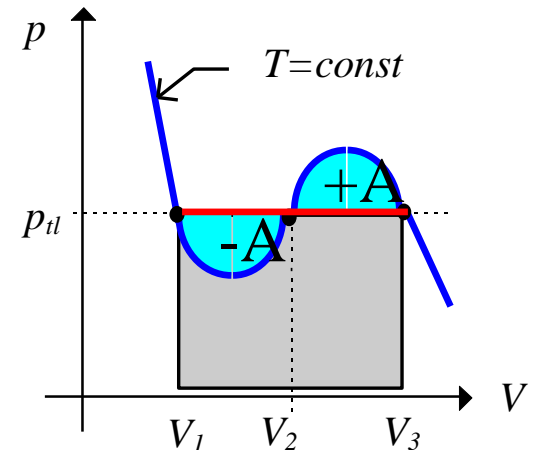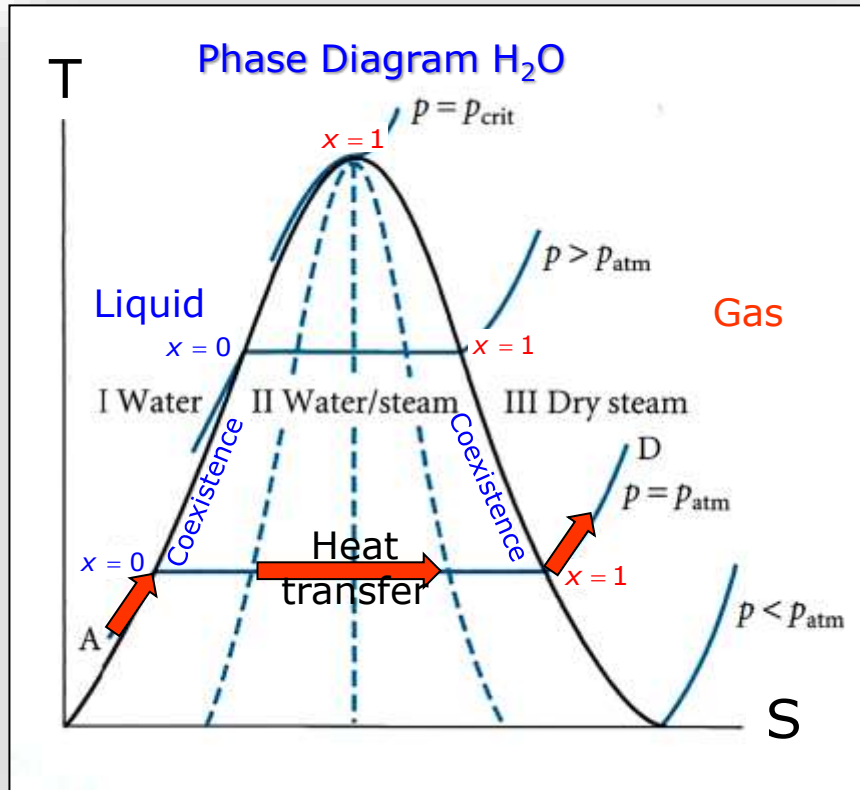
Compression leads to liquefaction.

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

Maxwell Construction

p

$T=const$

$+A$

$-A$

p_{tl}

V

V_1 V_2 V_3

Steam: Driving Gas for TD Engines

After Andrews & Jelley

Phase Diagram H_2O

T

$p = p_{crit}$

$x = 1$

$p > p_{atm}$

Liquid

$x = 0$ $x = 1$

Gas

I Water   II Water/steam   III Dry steam

Coexistence   Coexistence

$p = p_{atm}$

D

$x = 0$ Heat transfer $x = 1$

A

$p < p_{atm}$

S

To use steam as driving gas for thermal engines, energy has to be transferred to water at T_I (e.g., 25^0C)

1) to heat it to (100^0C)
2) to evaporate H_2O (@ 100^0C) ,
3) to heat the vapor $100^0C \rightarrow T_h$

p = 1 atm *(bar)= 101.33 kN/m²*
$\rightarrow$ Water boils @ at 100^0C
$\rightarrow$ Need *419 kJ/kg H_2O* to heat water from *0^0C* to *T= 100^0C*.

$\rightarrow$ @ *101.33 kN/m²)* and *100^0C*
Specific enthalpy H_2O:
     $h_{water}(100^0C)$ = 419 kJ/kg.
Specific enthalpy of evaporation:
     $h_{evap}(100^0C)$= 2,257 kJ/kg
(not needed for ideal gas):

Total heat required at *p=const.* to convert H_2O to steam @100^0C :

$h_{steam}(100^0C)$ = (419 + 2,257)kJ/kg = 2,676 kJ/kg = 2.676 (MJ/kg) = 0.74 kWh/kg

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

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

Internal Energy of Real Gases

Ar-Ar Lennard-Jones Potential
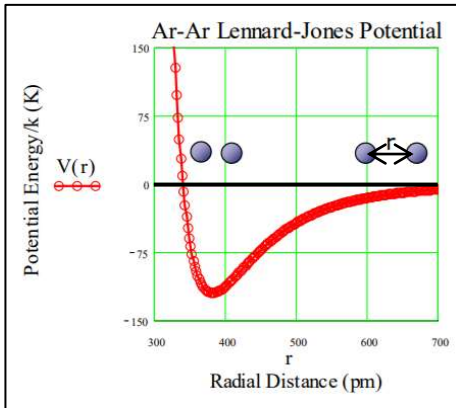
Effect of interaction on internal energy $U_{RG}(n,V,T)$.
What to expect?
Evaluate: use knowledge $\boxed{U(n,V,T)\xrightarrow[V\to\infty]{}U_{IG}(n,V,T)}$

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

Express in terms of
EoS→ {V, p, T}

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

See later and
Kondepudi, Ch.5

Generic real-gas EoS

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

van der Waals EoS

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

W. Udo Schröder, 2021

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	1.36
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

Ar-Ar Lennard-Jones Potential

Potential Energy/k (K)

V(r)

Radial Distance (pm)
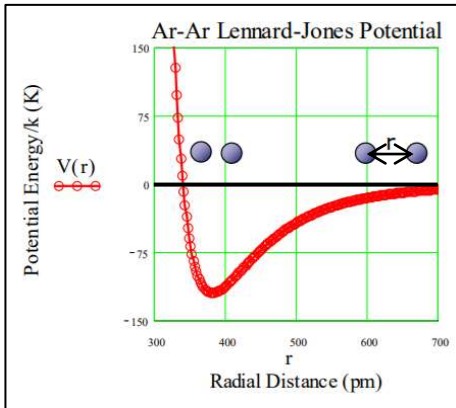
Effect of interaction on internal energy $U_{RG}(n,V,T)$.
Use knowledge

$$U(n,V,T) \xrightarrow[V \to \infty]{} U_{IG}(n,V,T)$$

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

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

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

Heat Capacity

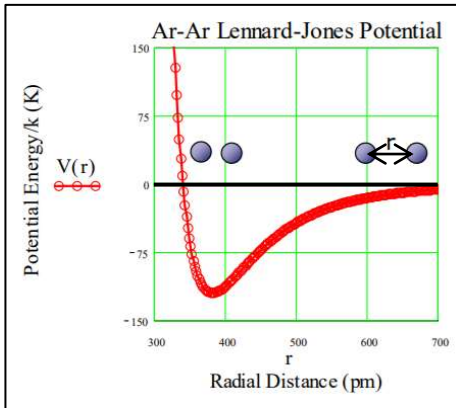$$C_V = C_{V,IG} - \frac{\partial}{\partial T} \int_V^\infty T^2 \left(\frac{\partial}{\partial V} \frac{p}{T} \right)_V dV \qquad C_V = C_{V,IG} - \int_V^\infty T \left(\frac{\partial^2 p}{\partial T^2} \right)_V dV$$

$$\Rightarrow vdW \; EoS: \partial^2 p / \partial T^2 = 0 \to \boxed{C_V^{vdW} = C_{V,IG}}$$

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

Ar-Ar Lennard-Jones Potential

$$A(n,V,T) \xrightarrow[V \to \infty]{} A_{IG}(n,V,T)$$

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

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

Generic real-gas EoS

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

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

Helmholtz free energy

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

Gibbs free energy

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

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

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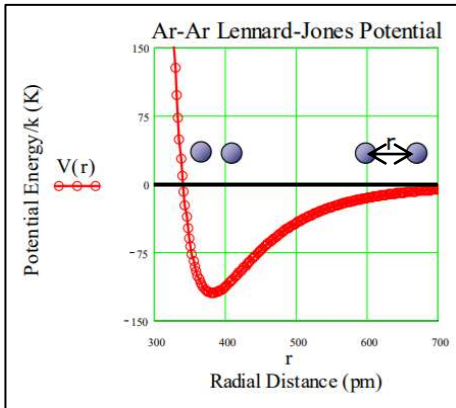
n moles/ particles

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**

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

Chemical Potential of Real Gases: p Dependence

Ar-Ar Lennard-Jones Potential

Potential Energy/k (K)

$V(r)$

r

Radial Distance (pm)

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: $Ln\left(\frac{f}{p}\right) := \int_0^p \frac{(Z-1)}{p}\, dp;$ $Lim_{p\to 0}(f/p) = 1$
"Activity" $a := f/p$

$$Ln\left(\frac{f}{p}\right) \approx B'(T) \cdot p + \frac{1}{2} C'(T) \cdot p^2 + ... \rightarrow$$

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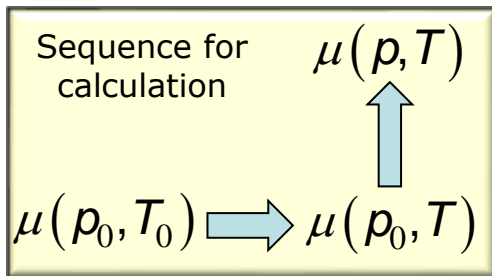
$$\mu(p,T) \approx \mu_{IG}(p_0,T) + R \cdot T \cdot \left[B'(T) \cdot p + \frac{1}{2} C'(T) \cdot p^2 \right]$$

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 $\boxed{\Delta G_f^0 = \mu(p_0,T_0)}$
@ $p_0 = 1bar$, $T_0 = 298.15K$ → need to scale up. Since μ → **G(p,T):**

Sequence for calculation $\mu(p,T)$

$\mu(p_0,T_0) \Longrightarrow \mu(p_0,T)$

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

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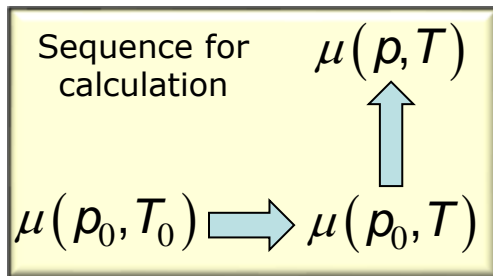
Gibbs-Helmholtz Equation

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

Parameterizing the Chemical Potential

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

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

Sequence for calculation
$$\mu(p,T)$$

$$\mu(p_0,T_0) \Longrightarrow \mu(p_0,T)$$

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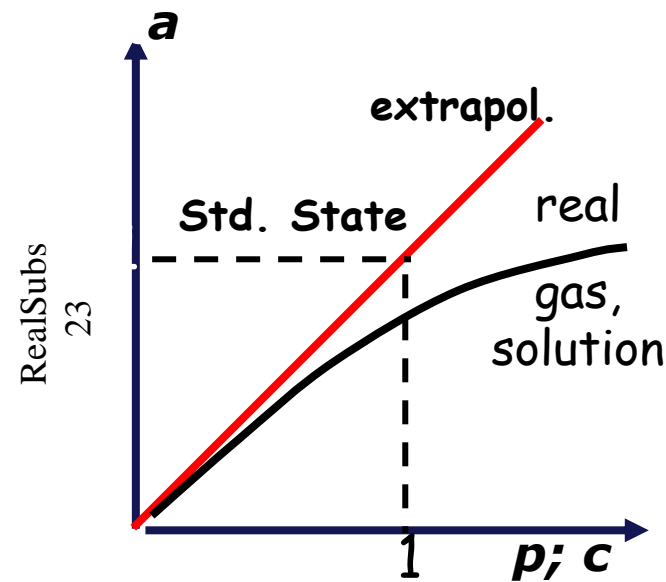
$$\mu(p,T) = \mu(p_0,T) + \int_{p_0}^p V(p',T)\,dp'$$

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

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

NIST Data Base

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

Phen Real Gases

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.

$Activity\ \ a:\ \ \ G(a) = G^o + nRT \cdot \ln(a)$

$G^0 = G(standard\ state)\ \ \ 1M$

$ideal\ gas\ a = p/1atm$

$real\ gas\ \ a = \gamma \cdot p\ \ \ \ \ \ \gamma = activity\ coefficient$

$pure\ solids\ or\ liquids\ \ a = 1$

$solutions\ a = \gamma \cdot c\ \ \ \ \ \ c = concentration\ (mol/L)$

$standard\ state:\ \ \ \ \ \ \gamma = 1\ like\ dilute\ solutions$

$solvent: a = \gamma \cdot x\ \ \ \ \ \ x = mole\ fraction$

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

$Pure\ solids\ and\ liquids: a_k \approx 1$

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

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 $\boxed{\mu_k^0(T) = \Delta G_f^0(k,T)}$

Equilibrium Constant (T)

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

Meaning of activity a_k : nominally replaces pressure in TD relations

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

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

Pure solids and liquids : $a_k \approx 1$

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