Agenda: TD Phenomenology of Real Matter, Gases etc.

- Fundamental ideal gas laws,
  - Equations of state (EoS)
  - Isothermal expansion/compression
  - Adiabatic expansion/compression

- Circular processes
  - Work, heat, and entropy in Carnot processes
  - Carnot, Kelvin/Clausius 2ndLTD
  - Thermodynamic driving potentials
  - Application chem reaction

- Equation of state of real matter
  - Van der Waals gas & other gas models, applications
  - Energy, activity, fugacity of real matter, gases & liquids
  - Phase equilibria

- Statistical Mechanics
  - Quantum statistics
  - Partition functions

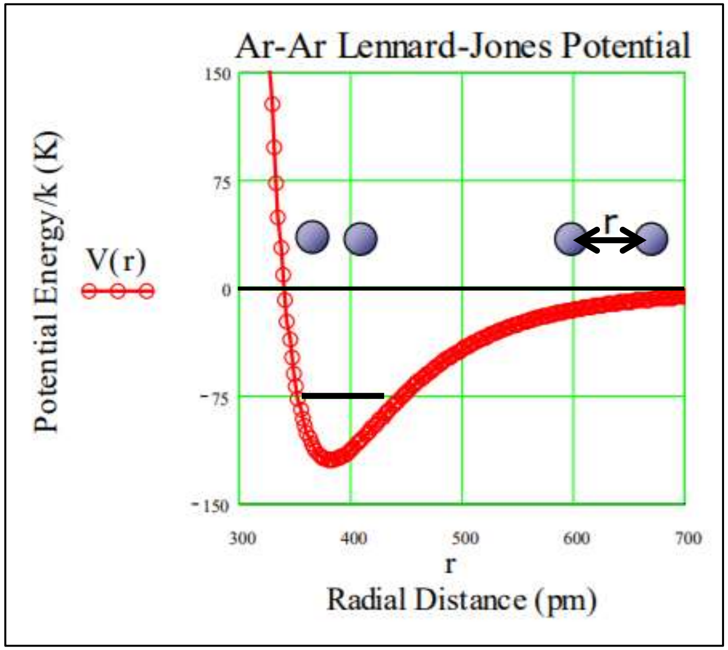
Reading Assignments
Weeks 7 & 8
LN IV.4-7:

Kondepudi Ch. 3.5-3.7, 6.1-6.3, 7.

McQuarrie & Simon
Ch. 5, 6

Math Chapter B, C

Real Substances



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

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)

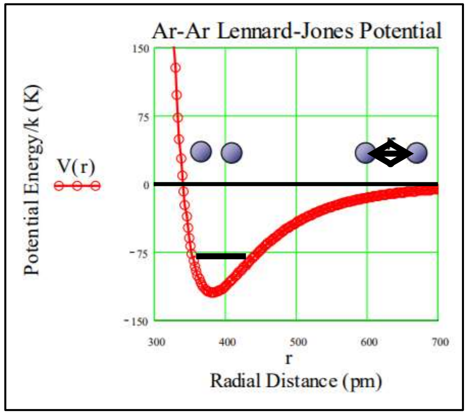
→ Real gas molecules interact with each other → motion is more or less free depending on density, pressure, temperature

→ 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



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,

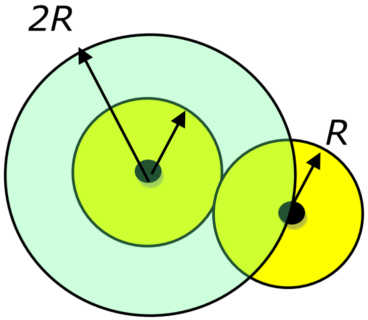
$$\Delta V = 8\cdot\upsilon \quad \text{with } \upsilon = \frac{4\pi}{3}\cdot R^3$$

Effective volume for *N* particles: $V \rightarrow V_{eff} = V \underbrace{-8\cdot N\cdot\upsilon}_{\Delta V<0}$

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

Excluded Volume

Hard-sphere interactions

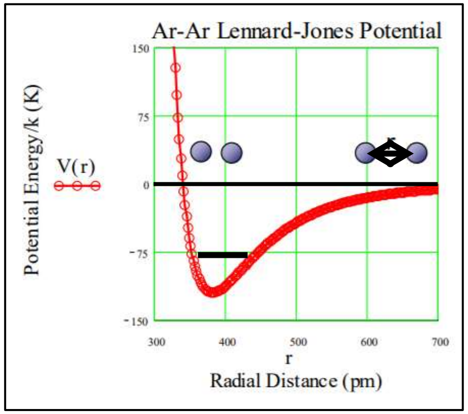


Effective density of real gas: $\rho_{eff} = N/V_{eff}$

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

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

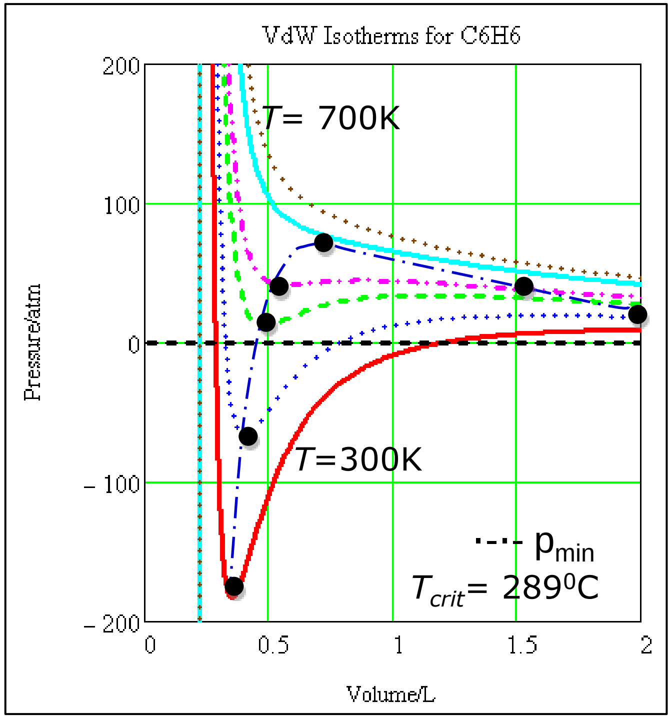
Effective Pressure of Real Gases/ vdW EoS



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

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

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



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

$$p_{meas} = p_{IG} + \Delta p$$

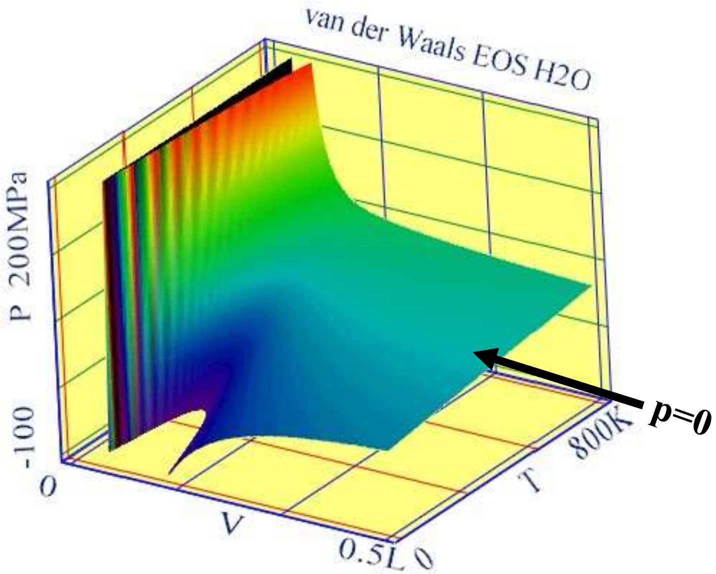
$$Nk_BT = p_{IG} \cdot V_{eff} = \left(p_{meas} - \Delta p\right) \cdot V \cdot \left(1 - 8\rho\upsilon\right)$$

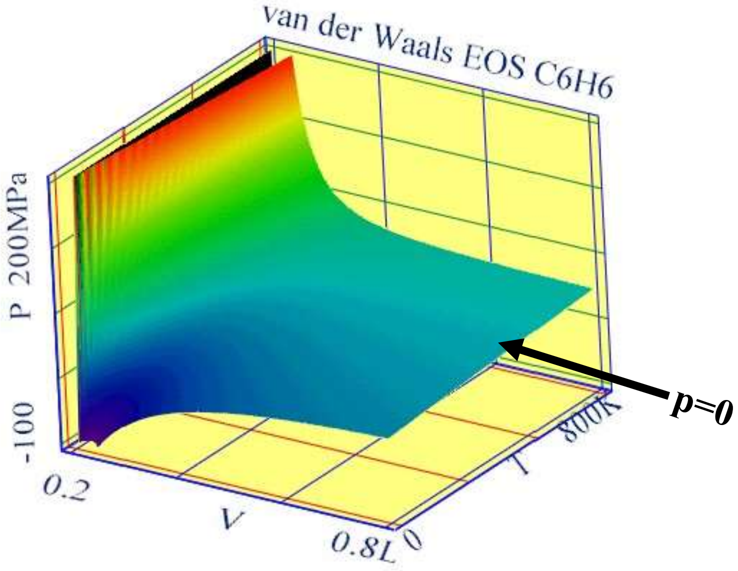
$$\boxed{\left(\underset{\uparrow}{p} + a\left(\frac{N}{V}\right)^2\right) \cdot \left(\underset{\uparrow}{V} - Nb\right) = Nk_BT}$$

van der Waals EoS for real gases

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

Real-Gas Equation of State





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

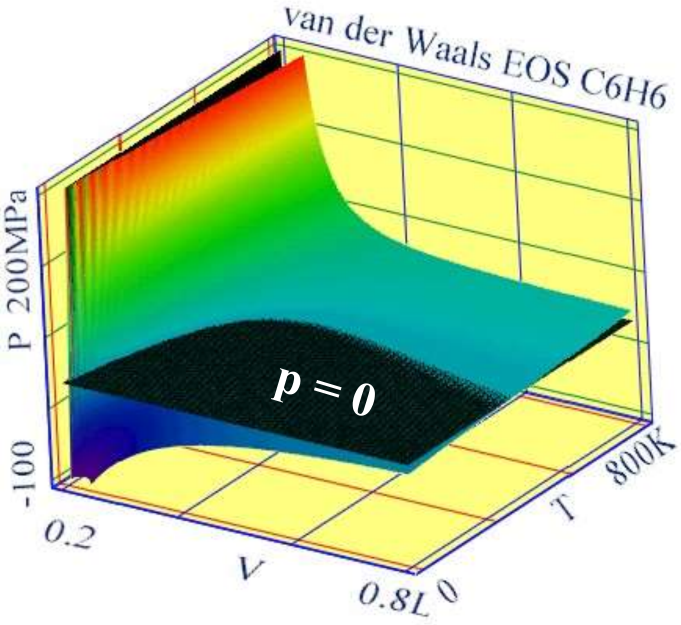
van der Waals: effects taken into account

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

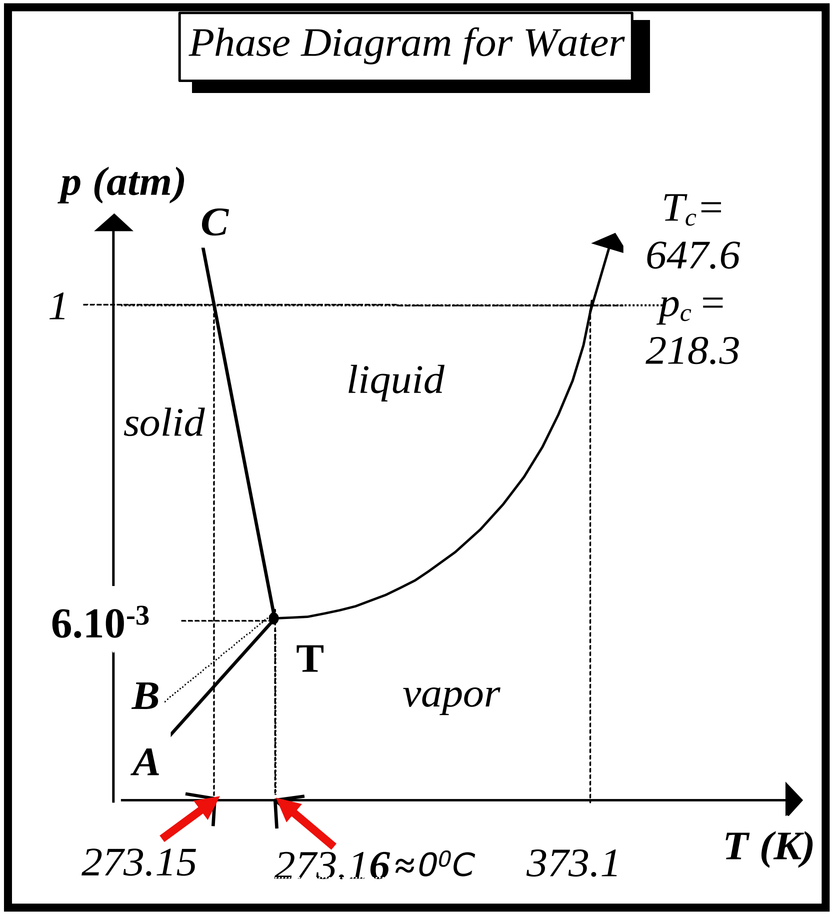
b) collisions between particles reduce the actual pressure, attractive interactions.

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

vdW EoS & Phases of Matter



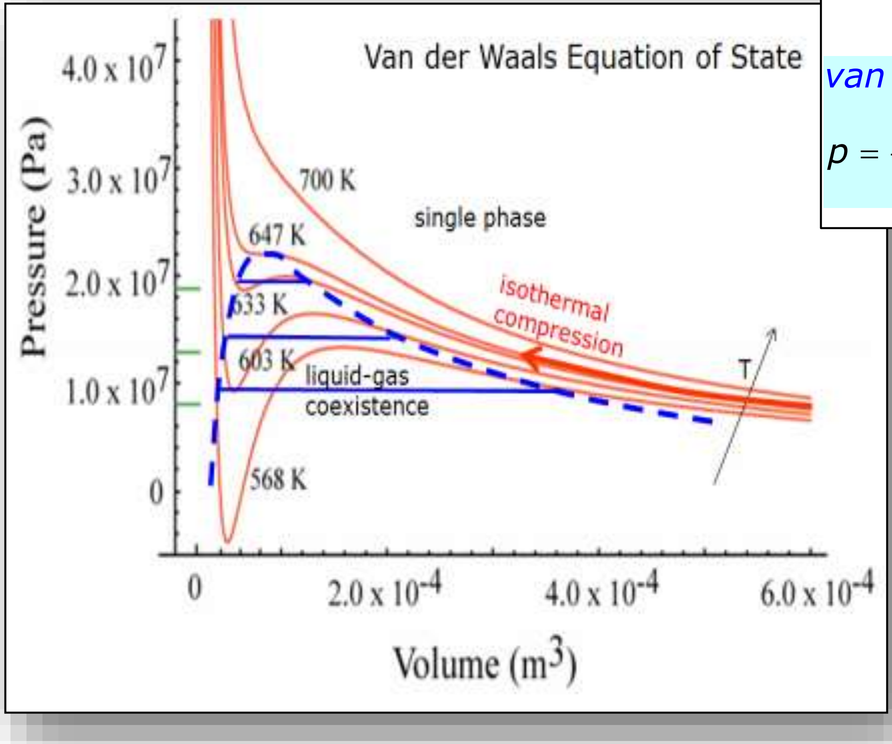
Shaded: negative pressures, substance does not exist as gas, liquefaction, liquid-gas coexistence, freezing to solid.



		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

Model 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

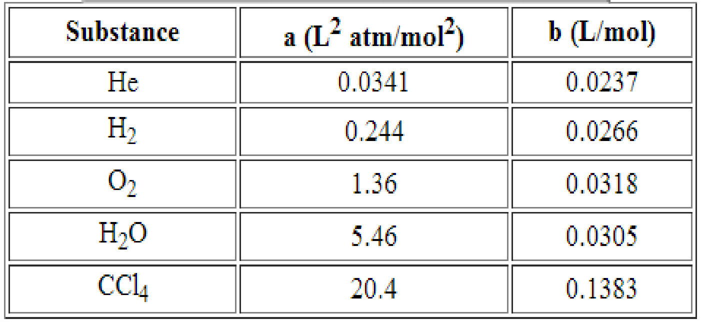
van der Waals EoS :

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

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_2O	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

Maxwell Construction Outlining Coexistence Region

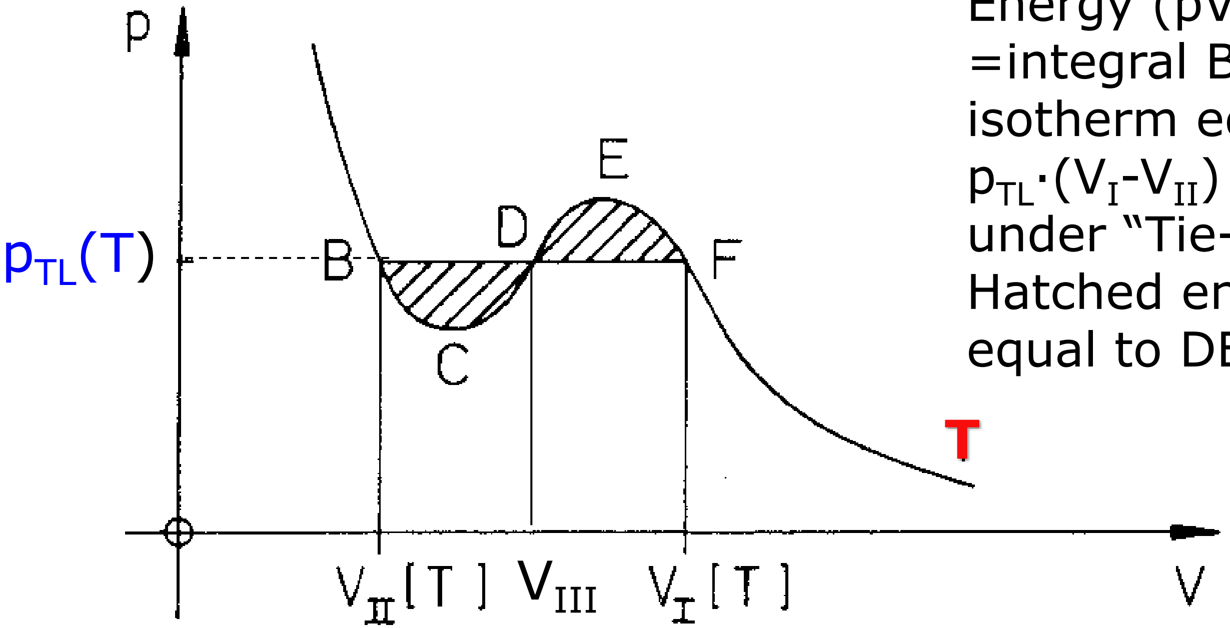
$$3p_rV_r^3 - \left(p_r + 8T_r\right)V_r^2 + p_r - 3 = 0$$

has 3 roots $V_r\left(p_r, T_r\right) \rightarrow$ *instability of configuration*

$\rightarrow$ *Change in phase to include clusterization, liquid droplets,*

Effects beyond the model space of consideration.

Htached unstable $p - V$ *region* $\rightarrow$ *coexistence of gas and liquid*



Maxwell Construction of P_{TL}
Energy (pV work)
=integral BCDEF along vdW isotherm equals rectangle $p_{TL} \cdot (V_I - V_{II})$
under "Tie-line" pressure P_{TL}.
Hatched energy regions BCD equal to DEF also defines P_{TL}.

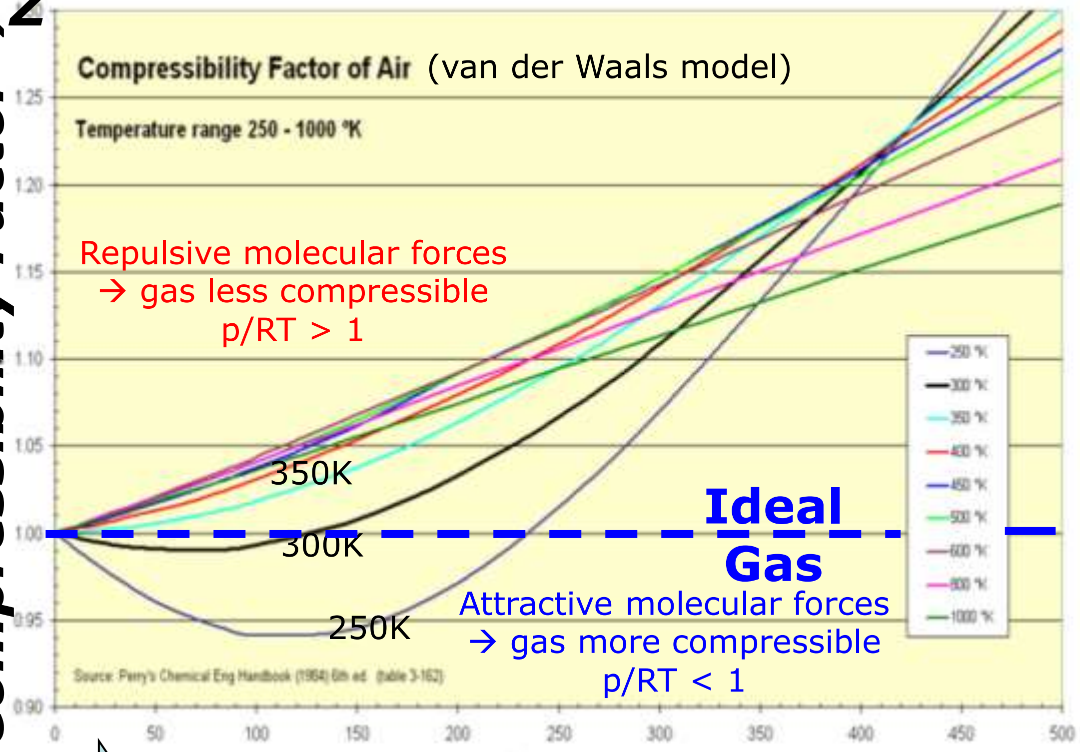
Compressibility Factor: Virial Expansions

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

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

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

Compressibility Factor → **Z**



Compressibility Factor of Air (van der Waals model)

Temperature range 250 - 1000 °K

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

Ideal Gas

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

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

Pressure (bar) →

Related:

Isothermal compressibility

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

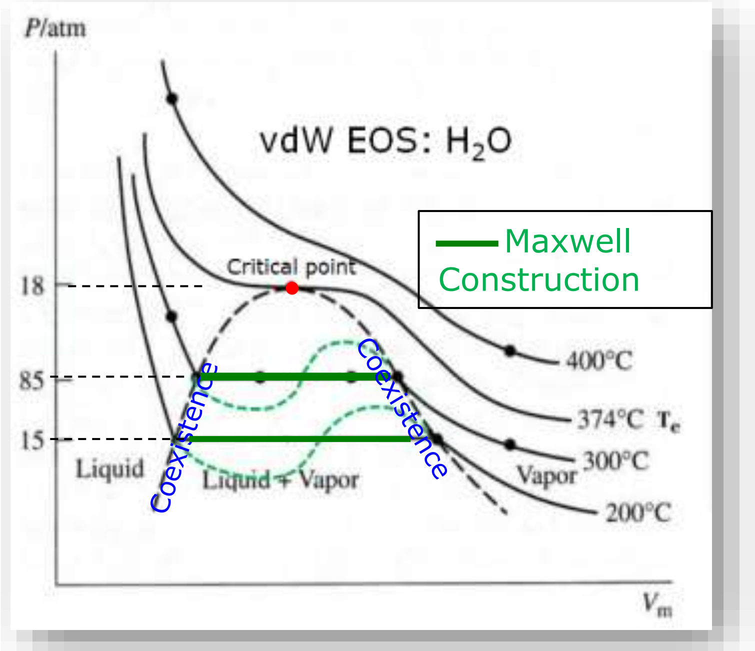
Volume expansion coefficient

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

Heat capacities

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

Law of Corresponding States



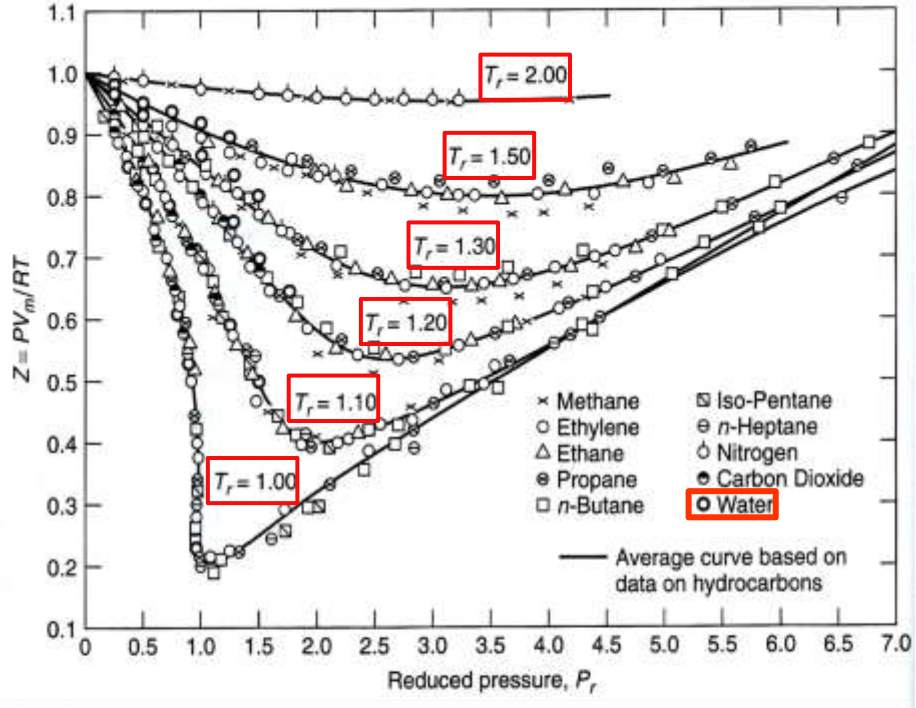
$$\left(p+\frac{n^2\cdot a}{V^2}\right)\cdot(V-n\cdot b)=n\cdot R\cdot T$$

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

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

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

Compressibility Factor $Z(P_r, T_r)$



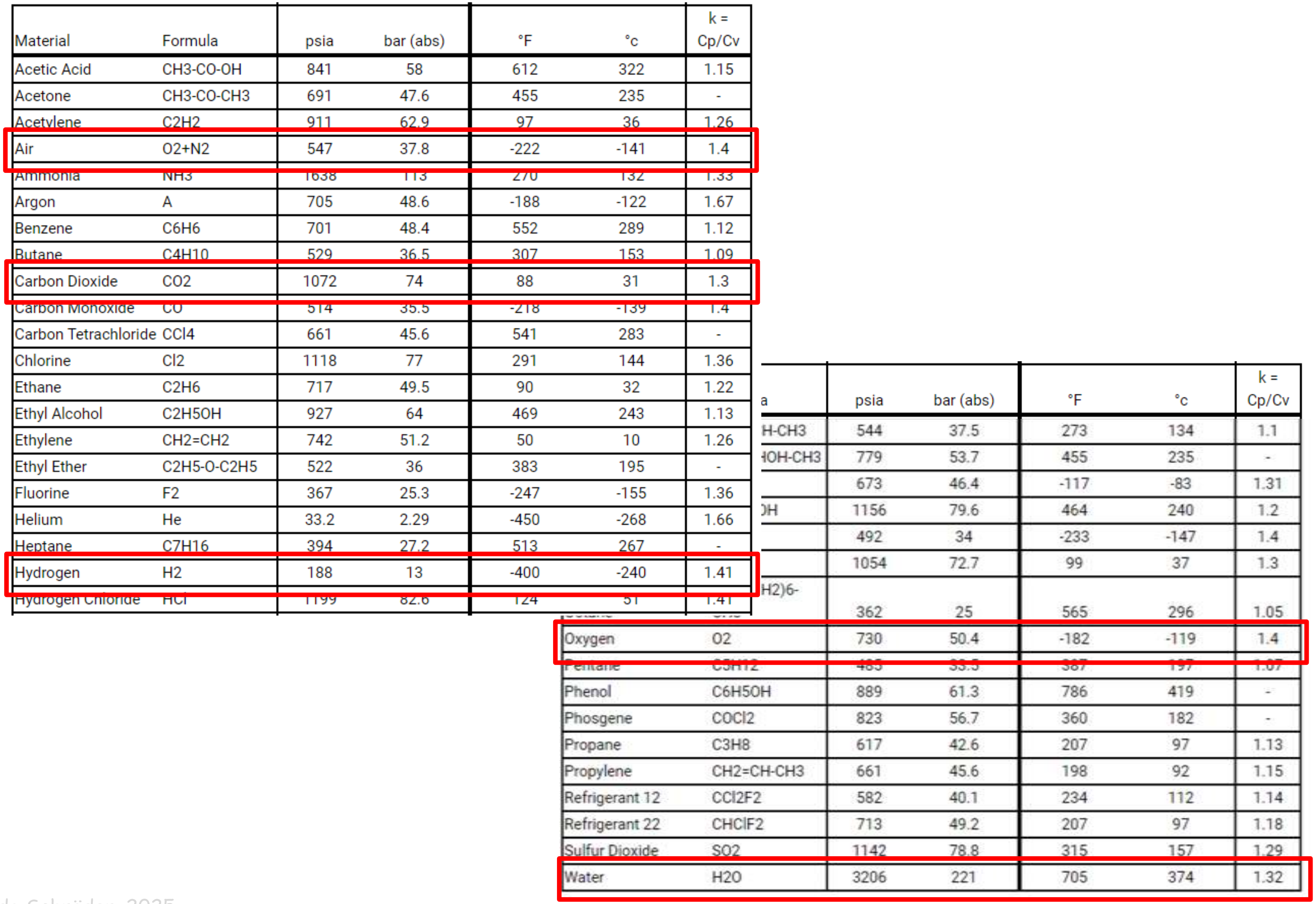
Industrial and Engineering Chemistry, Vol 38, ACS 1946

Law of Corresponding States

According to van der Waals, any gas:

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

Critical TD Parameters for Real Gases

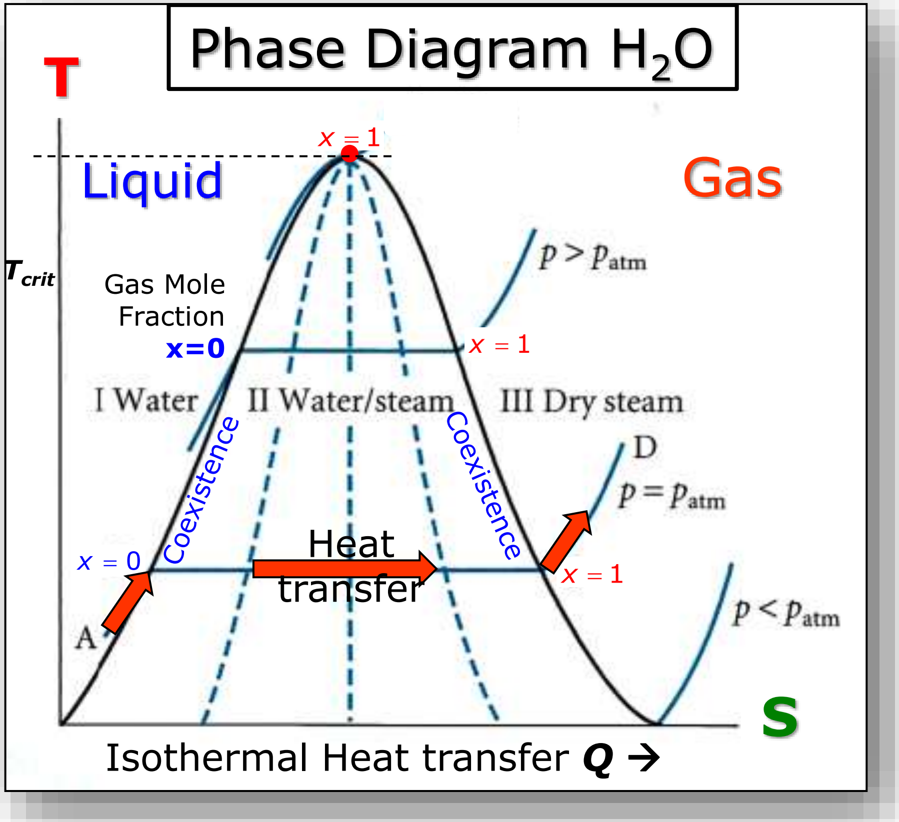


Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Acetic Acid	CH3-CO-OH	841	58	612	322	1.15
Acetone	CH3-CO-CH3	691	47.6	455	235	-
Acetylene	C2H2	911	62.9	97	36	1.26
Air	O2+N2	547	37.8	-222	-141	1.4
Ammonia	NH3	1638	113	270	132	1.33
Argon	A	705	48.6	-188	-122	1.67
Benzene	C6H6	701	48.4	552	289	1.12
Butane	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	32	1.22
Ethyl Alcohol	C2H5OH	927	64	469	243	1.13
Ethylene	CH2=CH2	742	51.2	50	10	1.26
Ethyl Ether	C2H5-O-C2H5	522	36	383	195	-
Fluorine	F2	367	25.3	-247	-155	1.36
Helium	He	33.2	2.29	-450	-268	1.66
Heptane	C7H16	394	27.2	513	267	-
Hydrogen	H2	188	13	-400	-240	1.41
Hydrogen Chloride	HCl	1199	82.6	124	51	1.41

	a	psia	bar (abs)	°F	°c	k = Cp/Cv
	H-CH3	544	37.5	273	134	1.1
	OH-CH3	779	53.7	455	235	-
		673	46.4	-117	-83	1.31
	H	1156	79.6	464	240	1.2
		492	34	-233	-147	1.4
		1054	72.7	99	37	1.3
	H2)6-	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

Steam: Driving Gas for Cyclic TD Engines

After Andrews & Jelley, Energy Science



To use dry steam (=gas) as work medium for thermal engines, energy must be transferred to water @ T_{liquid} (e.g., 25^0C), by:

1) heating it to (100^0C)

2) Evaporating liquid H_2O (@ 100^0C)

3) heating vapor from 100^0C → T_{high}

p = 1 atm *(1 bar)= 101.33 kN/m²*

→ Water boils @ at *100^0C*

→ Need *419 kJ/kg H_2O* to heat water from *0^0C* to *$T = 100^0C$*.

→ *@ 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):

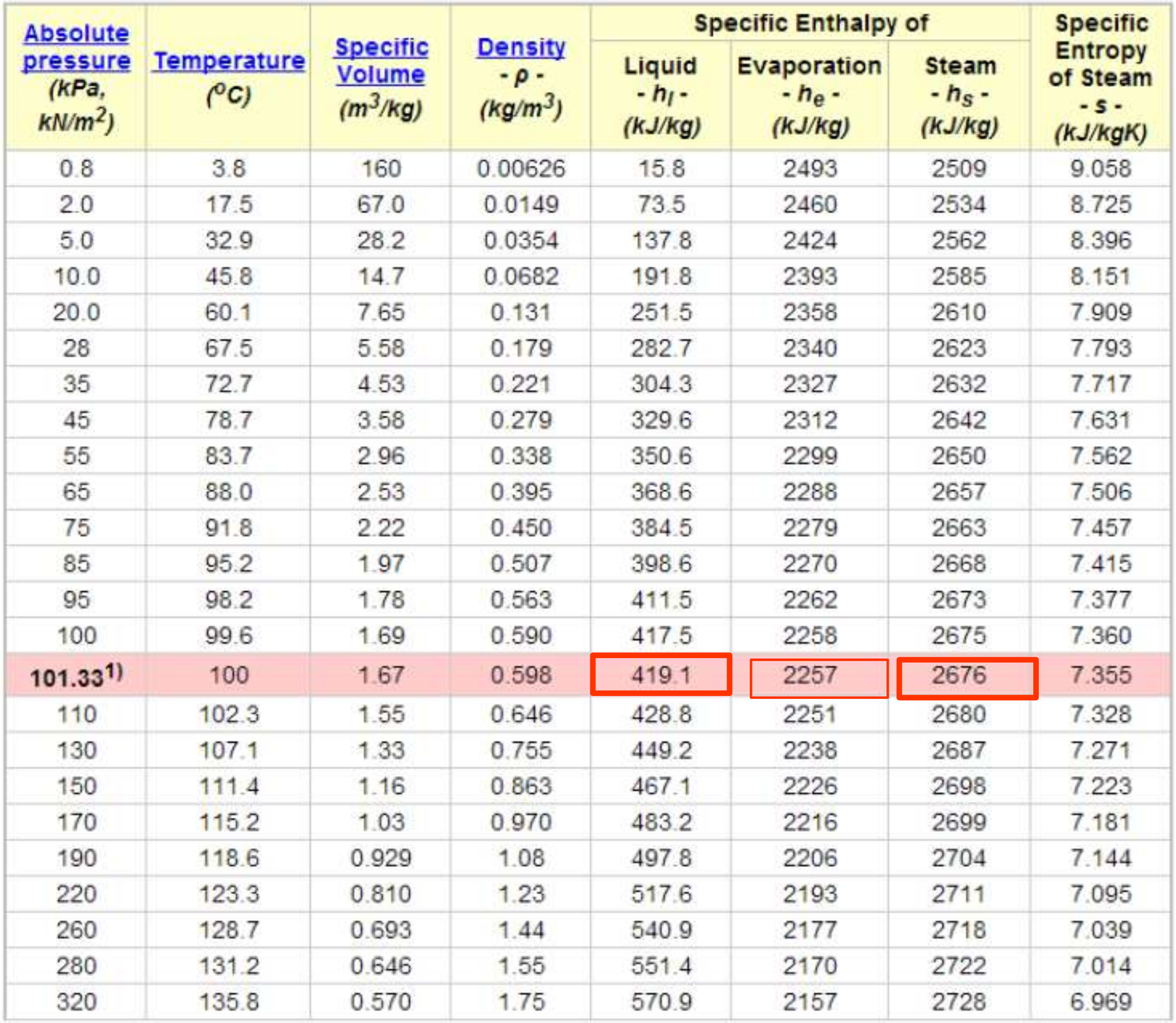
Total heat required at *p=const.* to convert H_2O to steam @*100^0C* :

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

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,..)*

Steam Tables



Absolute pressure (kPa, kN/m²)	Temperature (°C)	Specific Volume (m³/kg)	Density - ρ - (kg/m³)	Specific Enthalpy of Liquid - h_l - (kJ/kg)	Specific Enthalpy of Evaporation - h_e - (kJ/kg)	Specific Enthalpy of Steam - h_s - (kJ/kg)	Specific Entropy of Steam - s - (kJ/kgK)
0.8	3.8	160	0.00626	15.8	2493	2509	9.058
2.0	17.5	67.0	0.0149	73.5	2460	2534	8.725
5.0	32.9	28.2	0.0354	137.8	2424	2562	8.396
10.0	45.8	14.7	0.0682	191.8	2393	2585	8.151
20.0	60.1	7.65	0.131	251.5	2358	2610	7.909
28	67.5	5.58	0.179	282.7	2340	2623	7.793
35	72.7	4.53	0.221	304.3	2327	2632	7.717
45	78.7	3.58	0.279	329.6	2312	2642	7.631
55	83.7	2.96	0.338	350.6	2299	2650	7.562
65	88.0	2.53	0.395	368.6	2288	2657	7.506
75	91.8	2.22	0.450	384.5	2279	2663	7.457
85	95.2	1.97	0.507	398.6	2270	2668	7.415
95	98.2	1.78	0.563	411.5	2262	2673	7.377
100	99.6	1.69	0.590	417.5	2258	2675	7.360
101.33[1)]	100	1.67	0.598	419.1	2257	2676	7.355
110	102.3	1.55	0.646	428.8	2251	2680	7.328
130	107.1	1.33	0.755	449.2	2238	2687	7.271
150	111.4	1.16	0.863	467.1	2226	2698	7.223
170	115.2	1.03	0.970	483.2	2216	2699	7.181
190	118.6	0.929	1.08	497.8	2206	2704	7.144
220	123.3	0.810	1.23	517.6	2193	2711	7.095
260	128.7	0.693	1.44	540.9	2177	2718	7.039
280	131.2	0.646	1.55	551.4	2170	2722	7.014
320	135.8	0.570	1.75	570.9	2157	2728	6.969

Enthalpy

$$H(T) = H^0_{T_0=298K} + \Delta H(T)$$

$$\Delta H(T) = \int_{T_0}^{T} C_P(T')\,dT'$$

$$C_P(T) = C^0 + a\cdot T + b\cdot T^2 + \cdots$$

Parameters from data fits

p = 1 bar= 101.33 kN/m²

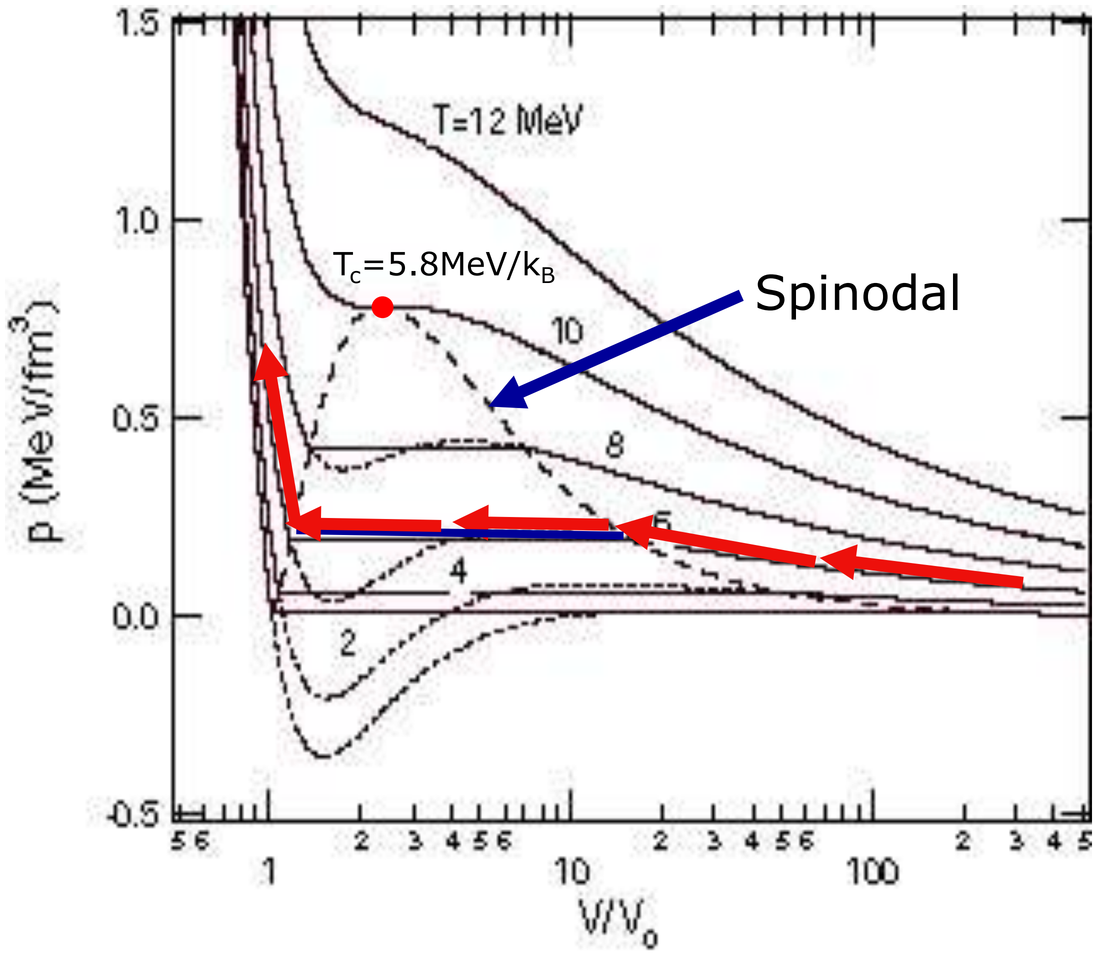
Water 0°C → 100°C.
→ 419 kJ/kg

→ Specific enthalpy H_2O:
$\boldsymbol{h}_{\boldsymbol{water}}(100^0C) = 419$ *kJ/kg*.

Specific enthalpy of evaporation:
$\boldsymbol{h}_{\boldsymbol{evap}}(100^0C) = 2{,}257$ *kJ/kg*

$\boldsymbol{h}_{\boldsymbol{steam}}(100^0C) = 2.676$ *MJ/kg*

Real Gas of Nucleons



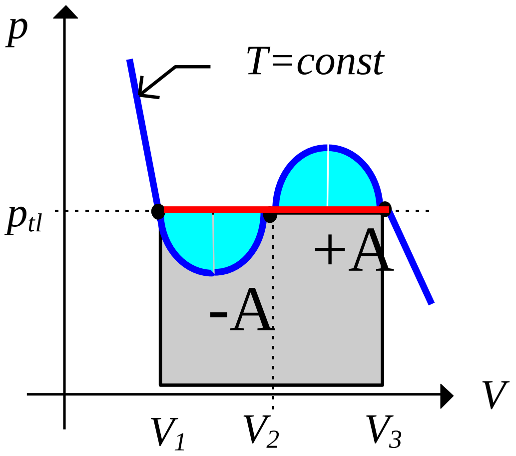
T_c=5.8MeV/k_B

Spinodal

Compression leads to liquefaction.

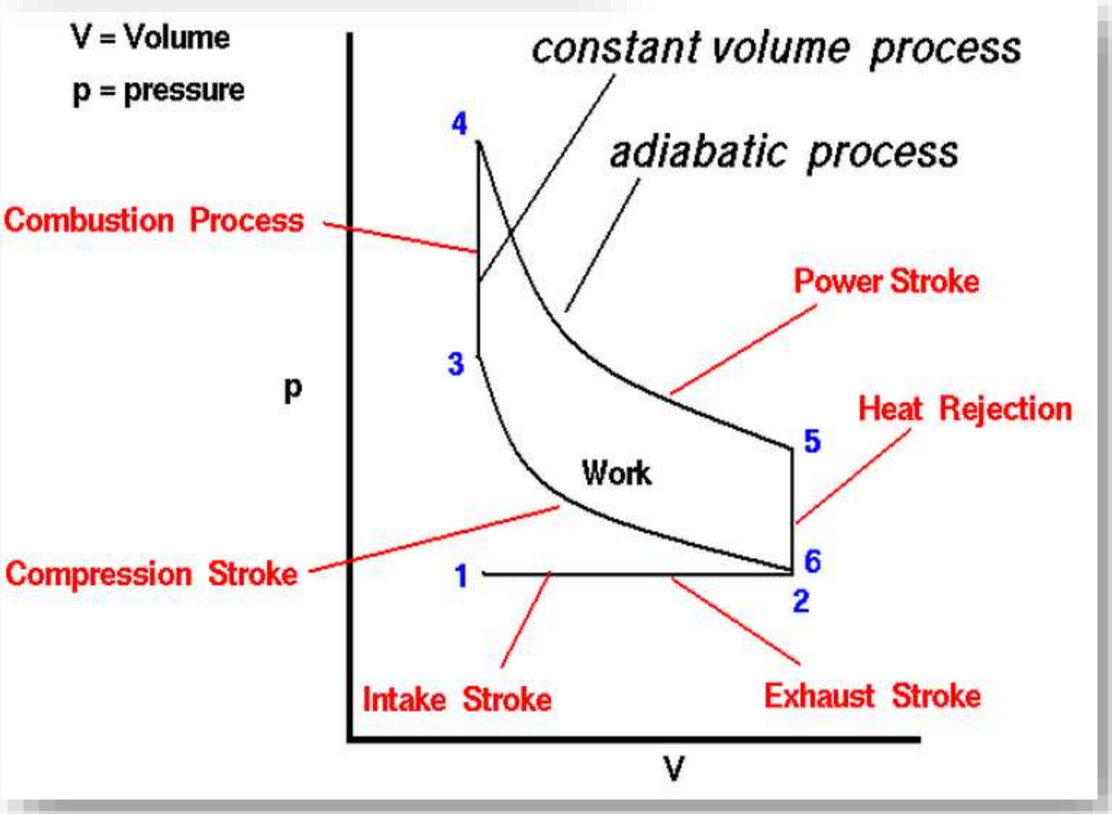
"Tie-line" pressure from Maxwell construction: +A=|-A|

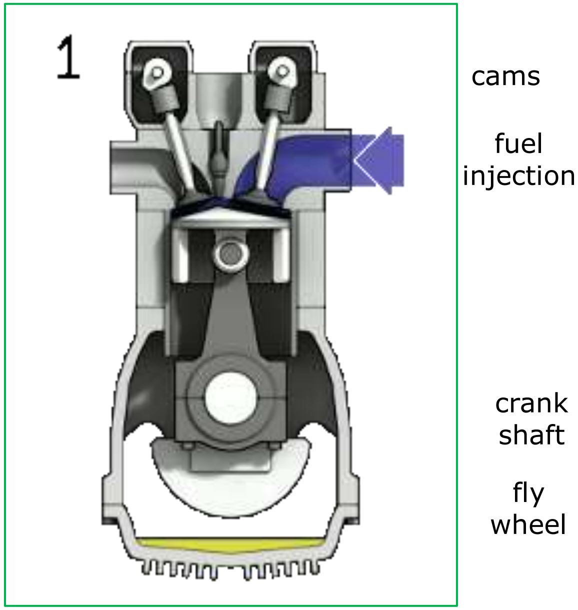
Maxwell Construction



Ideal Otto Cycle

1) Intake stroke (1→2), gasoline vapor and air drawn into engine.
2) Compression stroke (2→3) . *p,T* increase.
3) Combustion (spark) (3→4), short time, *V*= constant. Heat absorbed from high-*T* "reservoir".
4) Power stroke: expansion (4→5).
5) Valve exhaust: Valve opens, gas can escape.
6) Emission of heat (5→6) to *low-T reservoir.*
7) Exhaust stroke (2→1), piston evacuates cylinder.





Turbine for Gas Power Plants

SGT-800 Power generation 47.00MW(e)
Fuel: Natural gas*, Frequency: 50/60Hz
Electrical efficiency: 37.5%
Heat rate: 9,597kJ/kWh (9,096Btu/kWh)
Turbine speed: 6,608rpm
Compressor pressure ratio: 19:1
Exhaust gas flow: 131.5kg/s
Exhaust temperature: 544°C (1,011°F)
NOx emissions (with DLE, corrected to 15% O2 dry): ≤ 15ppmV

Available for different power outputs (5-375 MW), revolutions 3,000-17,000 rpm, 50/60 Hz electric.
Efficiencies 0.35- 0.60