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

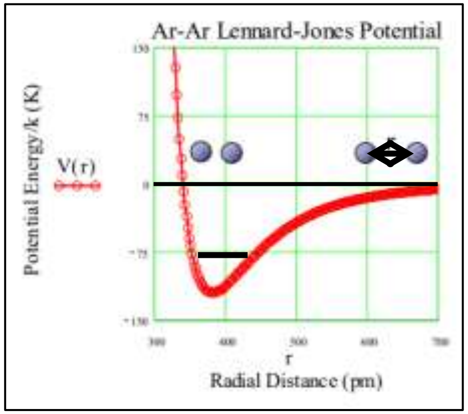
Reading Assignments
Weeks 7 & 8
LN IV.4-7:

Kondepudi Ch. 3.5-3.7, 5, 6.1-6.3, 7.

McQuarrie & Simon
Ch. 5, 6

Math Chapter B, C

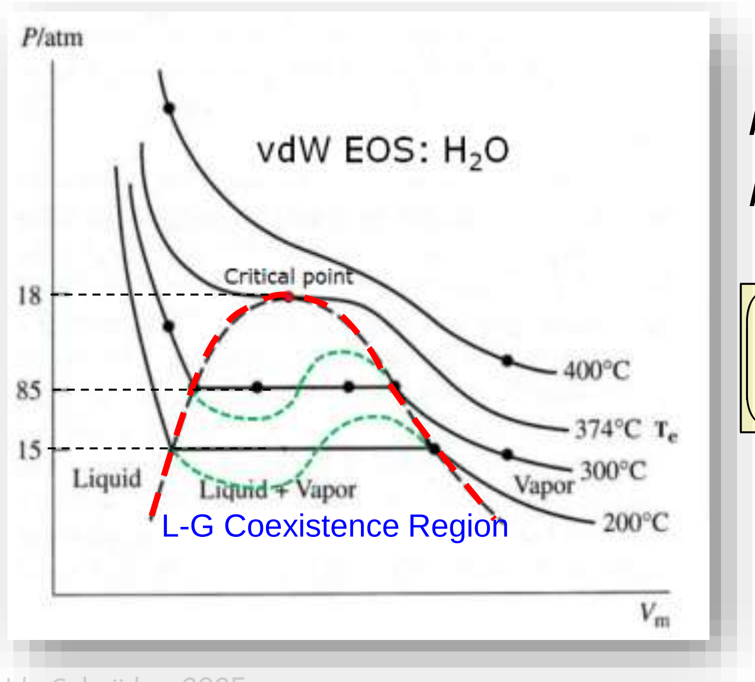
Effective Pressure of Real Gases/ vdW EoS



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

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

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



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

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

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

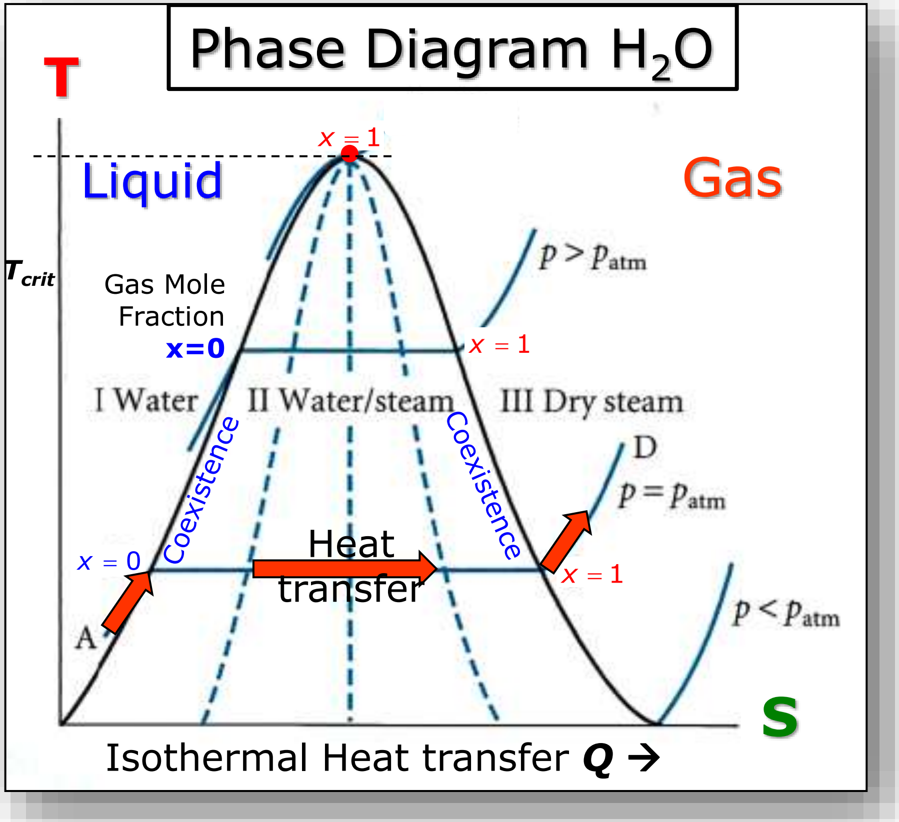
$$\boxed{\left(p + a\left(\frac{N}{V}\right)^2\right) \cdot \left(V - Nb\right) = Nk_B T}$$

van der Waals EoS
for real gases

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

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/m^2
→ Water boils @ at *100^0C*
→ Need *419 kJ/kg H_2O* to heat water from *0^0C* to *$T= 100^0C$*.

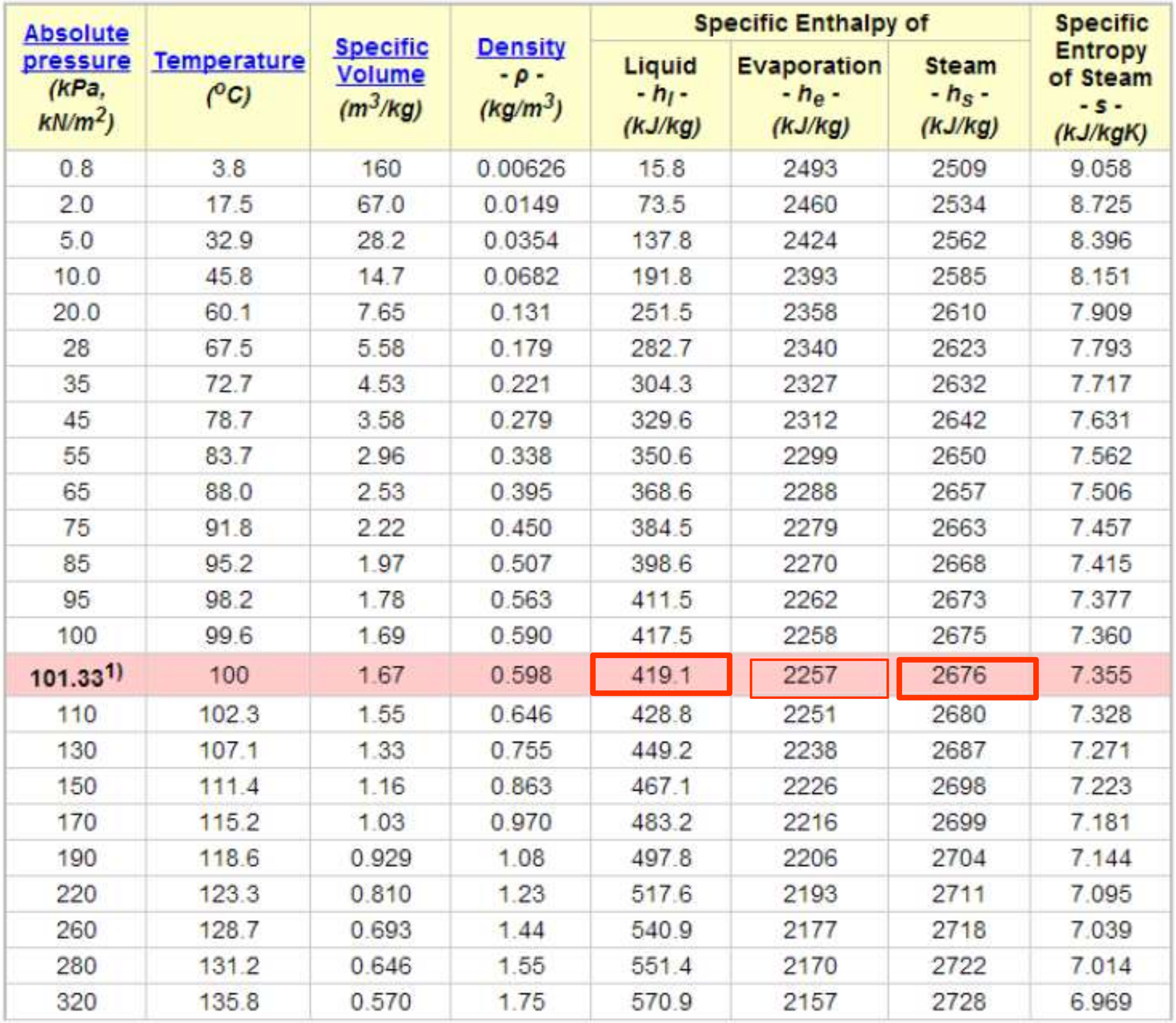
→ *@ 101.33 kN/m^2)* and *100^0C*
Specific enthalpy H_2O:
***h_{water}**(100^0C) = 419 kJ/kg*.
Specific enthalpy of evaporation:
***h_{evap}**(100^0C)= 2,257 kJ/kg*
(not needed for ideal gas):

Latent 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/m^2)	Temperature (^oC)	Specific Volume (m^3/kg)	Density - ρ - (kg/m^3)	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

1atm

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/m^2

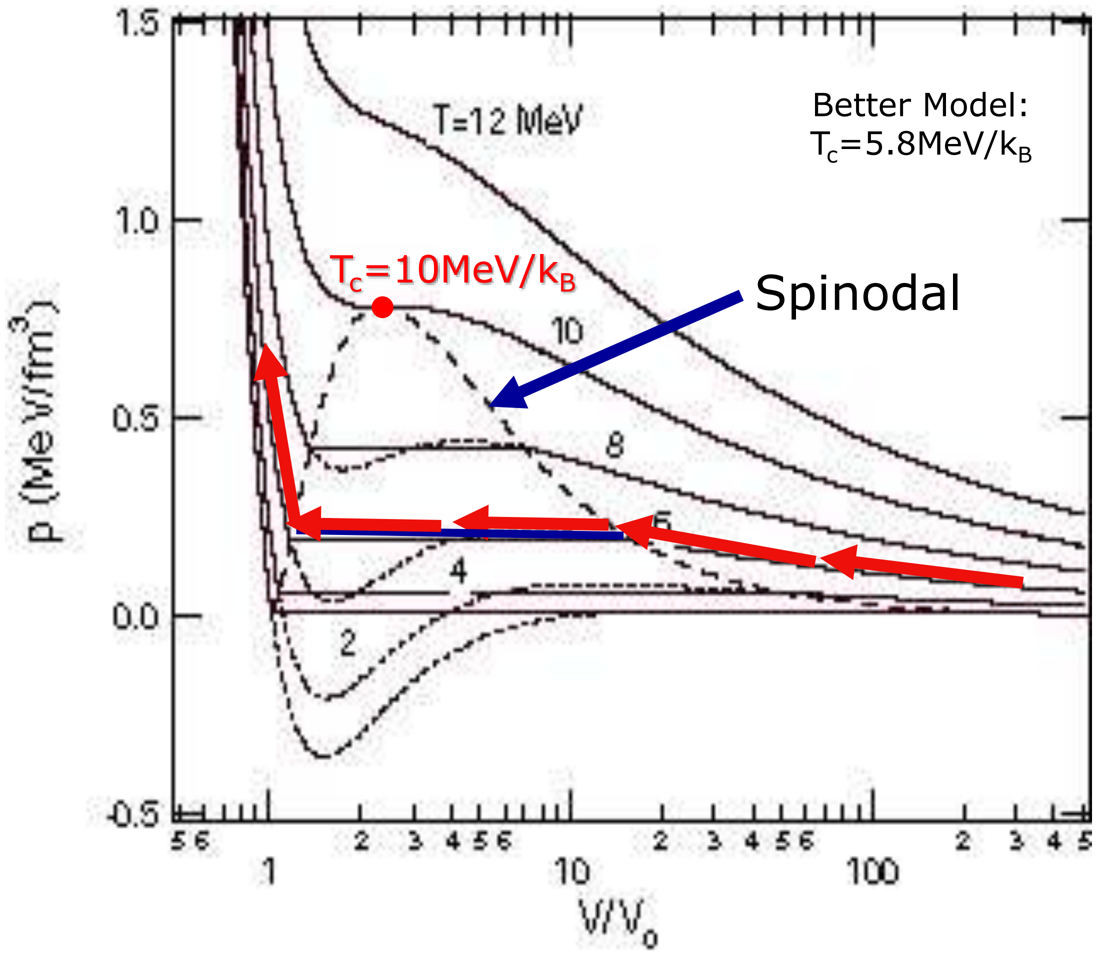
Water 0^0C → 100^0C.
→ 419 kJ/kg

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

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

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

Real Gas of Nucleons



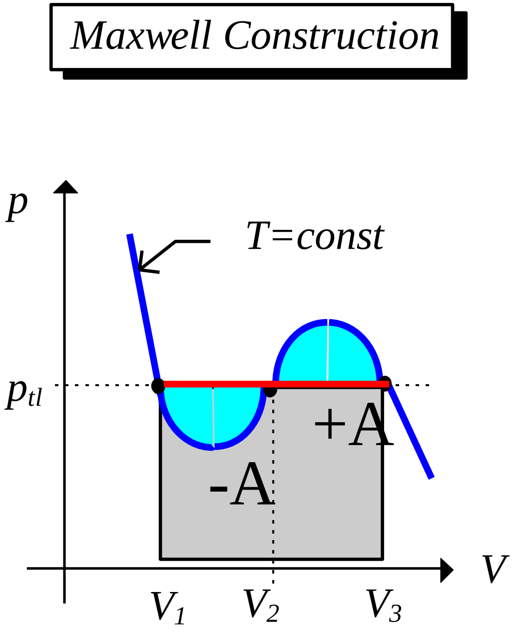
Better Model: $T_c=5.8\text{MeV}/k_B$

$T_c=10\text{MeV}/k_B$

Spinodal

Compression leads to liquefaction.

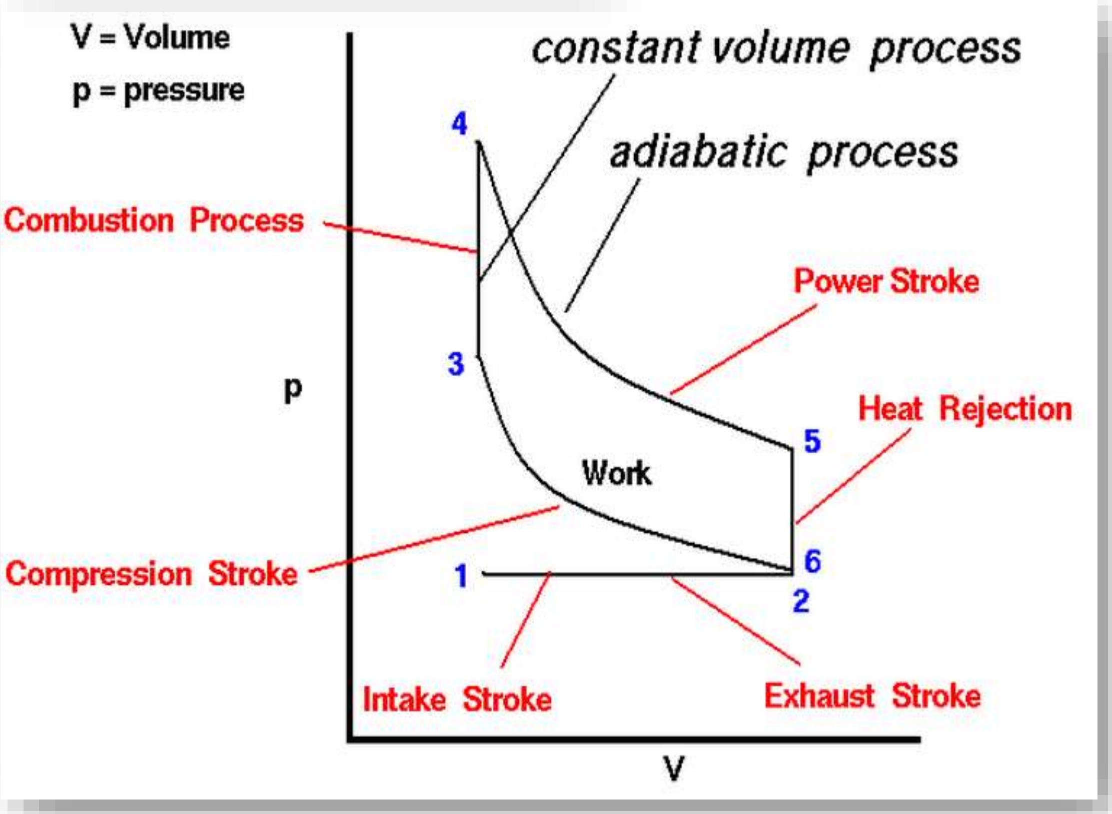
“Tie-line” pressure from Maxwell construction: +A=|-A|

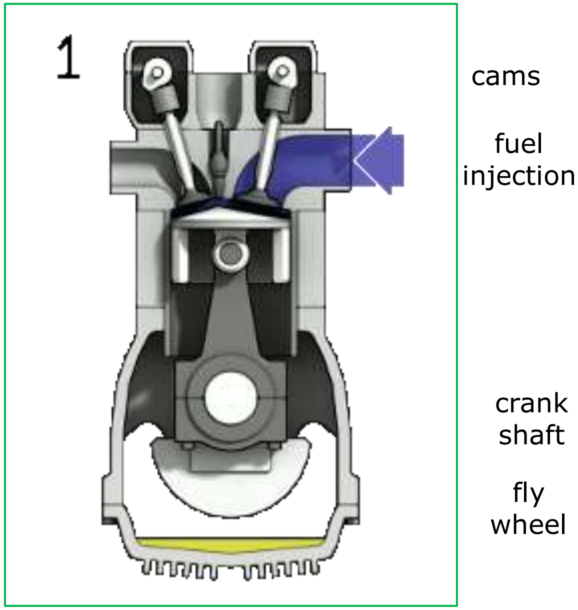


Maxwell Construction

Real Gas Internal Combustion Engines: 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 Natural-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

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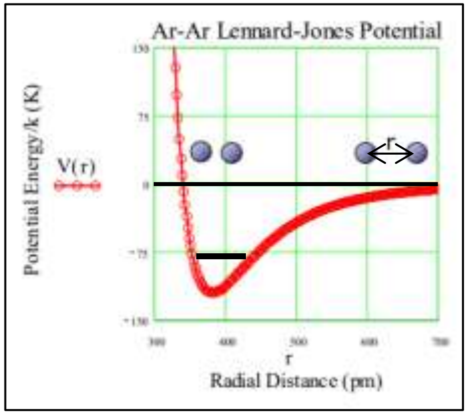
McQuarrie & Simon Ch. 5, 6

Math Chapter B, C

Internal Energy of Real Gases



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

What to expect?

Evaluate: use knowledge $\boxed{U(n,V,T)\xrightarrow[V\to\infty]{}U_{IG}(n,V,T)}$

$$U(n,V,T)=U_{IG}(n,V,T)+\Delta U_{RG}(n,V,T)\;<U_{IG}(n,V,T)$$

Estimate using vdW model: Generic real-gas EoS

$$p_{vdW}=\frac{n\cdot R}{(V-n\cdot b)}-\frac{n^2\cdot a}{V^2}\qquad with\ a>0;n=\#\,moles$$

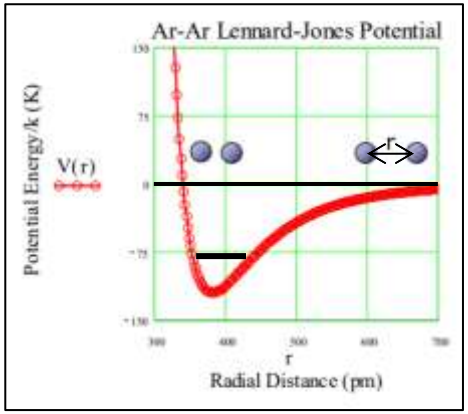
$$\boxed{\Delta p=p_{vdW}-p_{IG}\approx -a\cdot\frac{n^2}{V^2}\quad \text{with}\ \ a>0}$$

$$\boxed{\Delta U_{RG-IG}(n,V,T)\approx V\cdot\Delta p=-a\cdot\frac{n^2}{V}<0}$$

Real Gas Internal Energy (corrected for particle interactions)

$$\boxed{U(n,V,T)=U_{IG}(n,V,T)-a\cdot\frac{n^2}{V}}\xrightarrow[V\to\infty]{}U_{IG}(n,V,T)$$

Internal Energy of Real Gases



Effect of interaction on internal energy $U_{RG}(n,V,T)$.
Estimate using vdW model: Generic real-gas EoS

$$p_{vdW} = \frac{n\cdot R}{(V - n\cdot b)} - \frac{n^2\cdot a}{V^2} \qquad with\ a > 0; n = \#\,moles$$

$$\boxed{U_{vdW}(n,V,T) = U_{IG}(n,V,T) - a\cdot\frac{n^2}{V}} \xrightarrow[V\to\infty]{} U_{IG}(n,V,T)$$

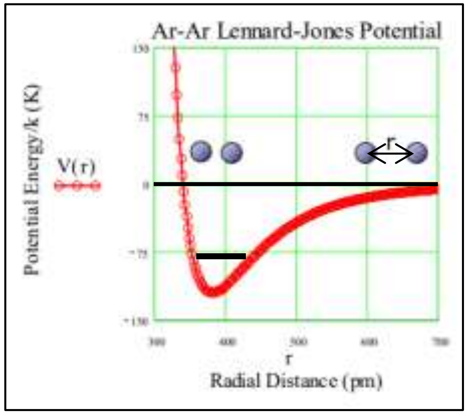
vdW Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = C_{V,IG} - \cancel{\left(\frac{\partial}{\partial T} a\frac{n^2}{V}\right)_V} = C_{V,IG} \to \boxed{C_V = C_{V,IG}}$$

vdW Heat Capacity

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

Free Energy of Real Gases: V and p Dependence



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

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

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

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

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

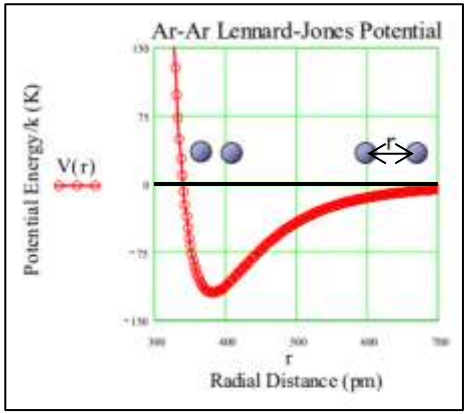
n moles or particles

van der Waals EoS $$A_{vdW}(n,V,T)=A_{IG}(n,V,T)-a\left(\frac{n}{V}\right)^2\cdot V-n\cdot R\cdot T\cdot Ln\left(\frac{V-n\cdot b}{V}\right)$$

solve ***A*** for ***S*** $$S_{vdW}=\frac{-1}{T}\cdot(A_{vdW}-U_{vdW})=n\cdot\left[s_0+C_V\cdot Ln\left(\frac{T}{T_0}\right)+R\cdot Ln\left(\frac{(V-n\cdot b)}{V}\right)\right]$$

$$\boxed{\frac{5}{2}R}$$

Chemical Potential of Real Gases: *p* Dependence



Use **Compression Factor *Z*** and asymptotic equivalence of real and ideal gases, *G(p,T)*→

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

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

$$\mu(p,T) = \left[\mu_{IG}(p_0,T) + R\cdot T\cdot Ln\left(\frac{p_{IG}}{p_0}\right)\right] + R\cdot T\cdot\int_0^p \frac{(\mathbf{Z}-1)}{p'}dp'$$

=f(n,a,b)

Pressure equivalent "Fugacity" f: $Ln\left(\frac{f}{p}\right) := \int_0^p \frac{(\mathbf{Z}-1)}{p}dp;\quad \lim_{p\to 0}(f/p) = 1$

"*Activity*" $a := f/p$

Chemical potential

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

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

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.

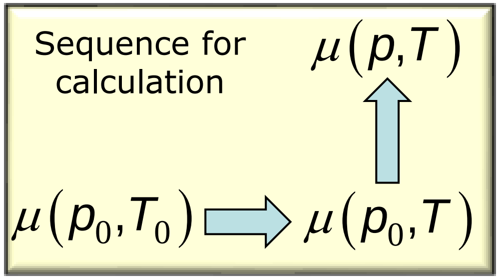
$$\mu(p,T) \approx \mu_{IG}(p_0,T) + R\cdot T\cdot\left[B'(T)\cdot p + \frac{1}{2}C'(T)\cdot p^2\right]$$

Chemical Potential of Real Gases: *T* Dependence

Calculate chemical potential of real gases from relations to ideal gases @$\boldsymbol{p_0, T_0}$

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

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 $\boldsymbol{\mu}$ → ***G(p,T):***



Sequence for calculation

$$\begin{tikzcd} & \mu(p,T) \\ \mu(p_0,T_0) \arrow[r] & \mu(p_0,T) \arrow[u] \end{tikzcd}$$

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

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

Gibbs-Helmholtz Equation

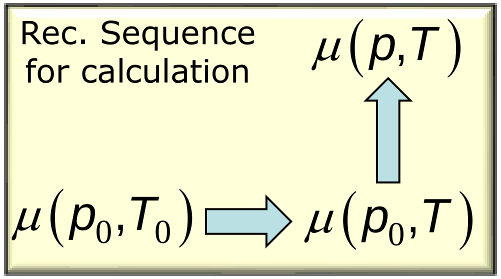
$$\boxed{\frac{\partial}{\partial T}\left(\frac{G}{T}\right) = -\frac{H}{T^2}}$$

Parameterizing the Chemical Potential

Calculate chemical potential of real gases from relations to ideal gases @$\boldsymbol{p}_0$

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

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



Rec. Sequence for calculation

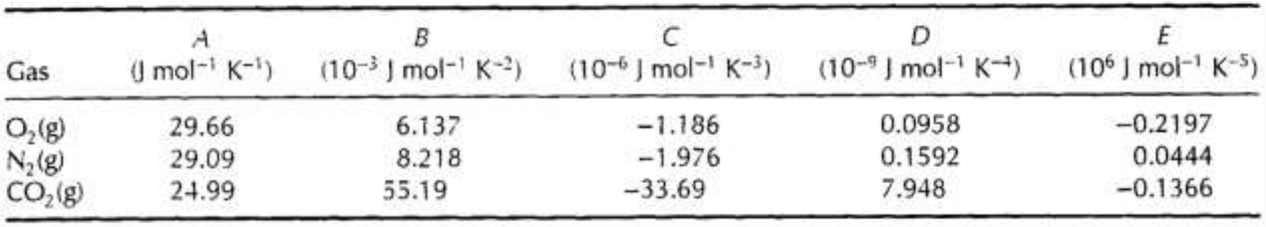
$$\mu(p_0,T_0)\Rightarrow\mu(p_0,T)\Rightarrow\mu(p,T)$$

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

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

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

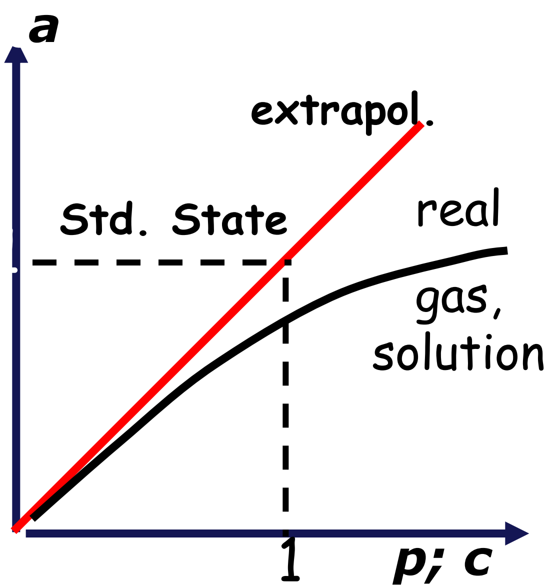
Molar heat capacity $C_p(T)=A+B\cdot T+C\cdot T^2+D\cdot T^3+E\cdot T^{-2}$



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

NIST Data Base

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.

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

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

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

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

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

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

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

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

$$Real\ gas\ a=\frac{f}{p}\rightarrow\text{"Fugacity" f:}\ Ln\left(\frac{f}{p}\right)=\int_{0}^{p}\frac{(Z-1)}{p}dp;$$

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

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

Gibbs Energy in Chemical Reactions

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

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

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: $Ln\left(\dfrac{f}{p}\right)=\int_0^p\dfrac{(Z-1)}{p}dp$;

Pure solids and liquids : $a_k\approx 1$

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