AA284a
Advanced Rocket Propulsion

Lecture 3
Review of Thermodynamics and Chemistry

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Review of Thermodynamics-Definitions

- System: A group of entities distinguished from its surroundings
  - Mass and energy transfer is allowed
  - Change of volume is allowed
  - Example: Human body
- Transfer quantities
  - Heat (transfer to the system): δQ
  - Work (done by the system): δW
  - Mass transfer: δM
- Definitions:
  - Open System: Mass transfer allowed
  - Closed System: Mass transfer **not** allowed
  - Adiabatic System: Heat transfer is **not** allowed

Reference on Thermodynamics: I. Klotz and R. Rosenberg, “Chemical Thermodynamics”

Review of Thermodynamics-Definitions

- State of the system: Quantify the status of the system
  - Extrinsic properties: E, H, G, M, N
  - Intrinsic properties: T, P, z, K
  - Extrinsic properties can be converted to intrinsic properties
    - Example: e=E/M
- Change of State:
  - Potential drives the system to change
  - When the potential diminishes system reaches an equilibrium.
- Mission of Thermodynamics
  - Governs the rules of change of state
  - Move from state A to state B is feasible or not for specified heat and mass transfer and work done
  - Thermodynamics does not answer the questions how fast or what is the exact form of the process.

Review of Thermodynamics-Laws

- **Zeroth Law:**
  - If A is in equilibrium with C and B is in equilibrium with C, than A and B must be in equilibrium.
- **First Law:**
  - Conservation of energy
  - Change in the internal energy must be equal to the heat added to the system minus the work done by the system

$$d\ e = \delta\ q - \delta\ w$$

  - For simple materials only work is the pressure work.

$$\delta\ w = P\ dv$$

  - In terms of enthalpy

$$d\ h = \delta\ q + v\ dP$$

e : Internal Energy
h : Enthalpy
q : Heat Transfer
w : Work Done
P : Pressure
v : Specific Volume

Review of Thermodynamics-Laws

- **Second Law:**
  - Reversible/Irreversible processes
    - Imagine a time dependent physical process governed by a set of equations
    - If these equations are invariant with regard to the sign of the time variable the process is reversible, else irreversible
  - There exists a system variable, entropy, with the following definition for a single component system

$$d\,s = \frac{\delta q}{T} \qquad d\,S = \frac{\delta Q}{T}$$

    - Explicit property
  - Second law of thermodynamics

$$d\,S_{universe} \geq 0$$

$S : Entropy$

$s : Specific\ Entropy$

$T : Temperature$

Review of Thermodynamics-Laws

- **Second Law:**
  - Or

$$d\ S_{system} + d\ S_{surroundings} \geq 0$$

  - For an isolated system

$$d\ S_{system} \geq 0$$

  - Entropy is a measure of “disorder” or lack of “information” on the possible microstates
  - Boltzmann’s Equation: $S = k\ \ln\left(N_{micro}\right)$
  - All real processes are irreversible

$k : Boltzmann's\ Cons.$

$N_{mic} : Number\ of\ Micro\ States$

- **Third Law:**
  - Planck’s Formulation: Value of entropy of a pure liquid or solid approaches zero at 0 K

Advanced Rocket Propulsion

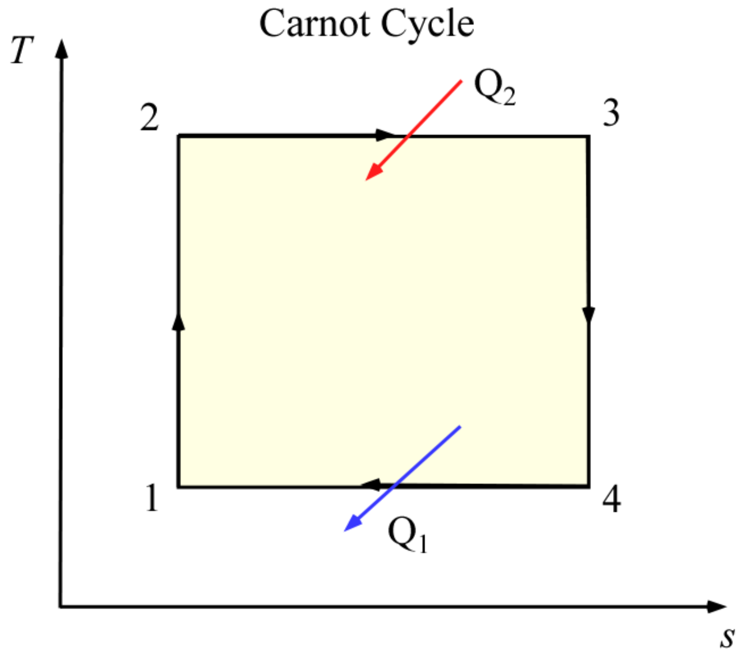
Review of Thermodynamics-Cycles

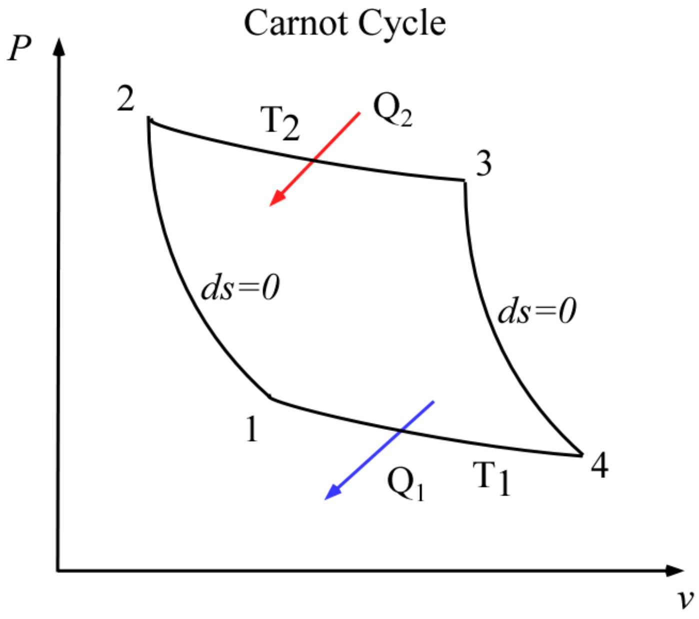
- Heat machines convert thermal energy into mechanical energy according to the laws of thermodynamics.
- Many machines work in cycles. Working fluid returns to the original state that it started.
- Carnot Cycle:
  - Two constant temperature heat transfer processes and two isentropic compression expansion processes
  - Carnot cycle efficiency: $$\eta_C = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_3}$$

$$\boxed{\eta : Efficiency}$$

- Bryton Cycle:
  - Two constant pressure heat transfer processes and two isentropic compression expansion processes
  - Bryton cycle efficiency: $$\eta_B = 1 - \frac{\Delta h_{cooling}}{\Delta h_{heating}} = 1 - \frac{T_1}{T_2} < 1 - \frac{T_1}{T_3}$$
- Cycle efficiency increases with increasing temperature ratio
- Carnot cycle is always the best efficiency heat machine operating between two specified temperature extremes (T_1 and T_3).

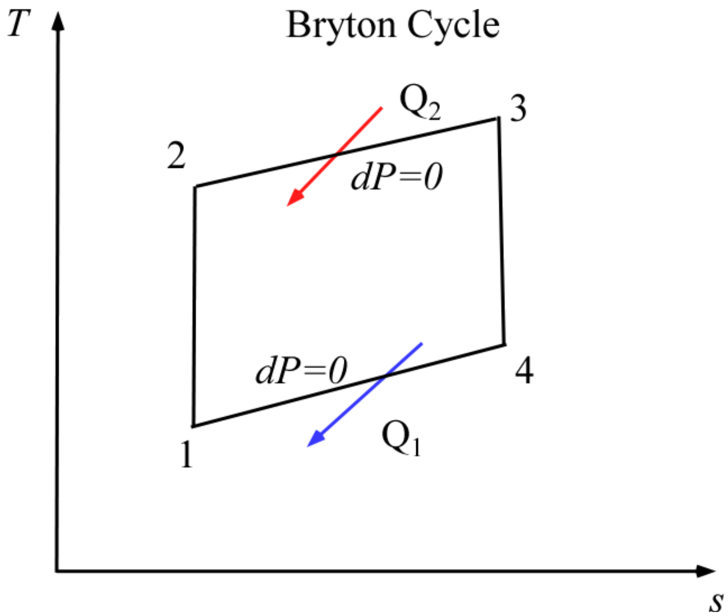
Review of Thermodynamics-Carnot Cycle

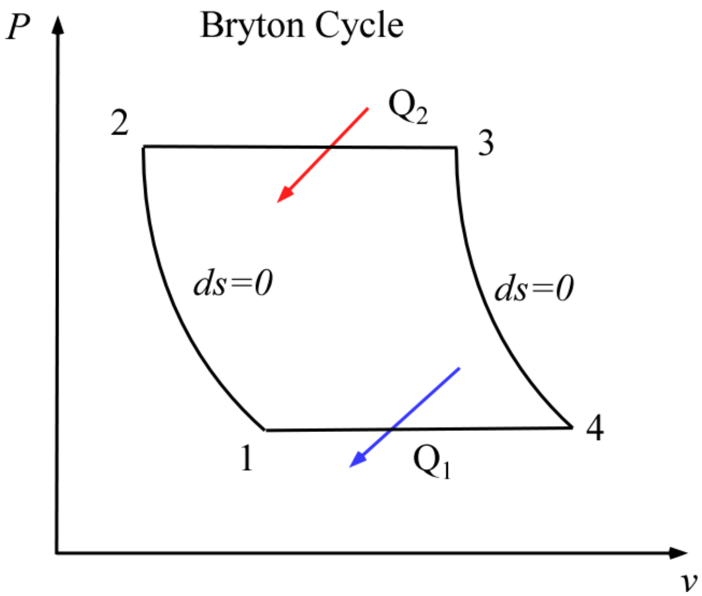

Carnot Cycle


Carnot Cycle

- Carnot Cycle Efficiency $\eta_C = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$
- Isothermal/Isentropic Branches: $s_1 - s_4 = -\frac{Q_1}{T_1}$ $s_3 - s_2 = \frac{Q_2}{T_2}$ $s_2 = s_1$ $s_3 = s_4$
- Combine: $\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$ $\Longrightarrow \eta_C = 1 - \frac{T_1}{T_2} = 1 - \frac{T_1}{T_3} = 1 - \frac{T_{cold}}{T_{hot}}$

Review of Thermodynamics - Bryton Cycle

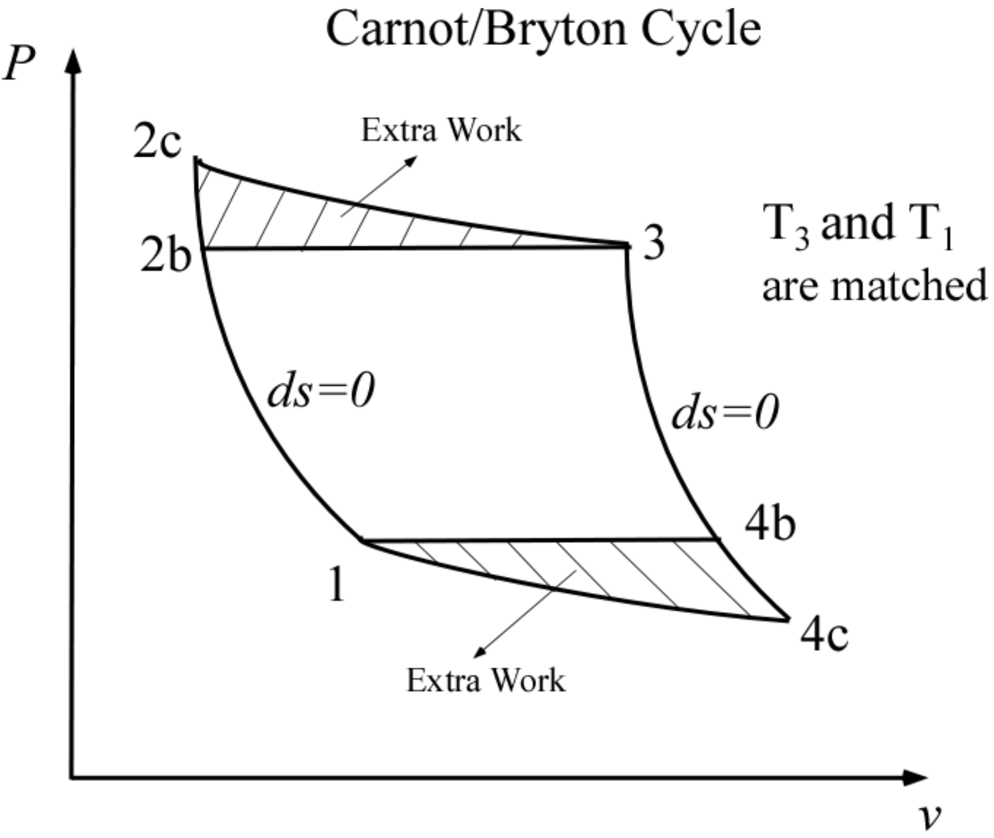




- Bryton Cycle Efficiency $\eta_B = 1 - \frac{Q_1}{Q_2} = 1 - \frac{h_4 - h_1}{h_3 - h_2}$
- Perfect Gas: $\eta_B = 1 - \frac{T_4 - T_1}{T_3 - T_2}$
- From Isentropic and Isobaric Branches: $\frac{T_4}{T_3} = \frac{T_1}{T_2}$

$$\Rightarrow \quad \eta_B = 1 - \frac{T_1}{T_2} \quad but \quad T_3 = T_{hot} > T_2$$

Review of Thermodynamics – Cycle Comparison



- Work done by the fluid

$$W = \oint P\,dv$$

- For the same extreme temperatures the Carnot cycle is more efficient than the Bryton cycle
- This conclusion is valid for all other cycles.
- Thus Carnot cycle sets the upper limit for the efficiency of a heat engine operating at two set temperatures
- Nonideal behavior is due to
  - Non-isothermal heat transfer
  - Non-isentropic expansion and compression

State Equation

- State equation relates the state variables of a substance to each other
- Gibb's Phase Rule:

Number of Phases + Independent Intensive Properties

=

2 + Number of Components

(P + V = C +2)

  - Examples
    - If P=1 and C=1, V=2 (One phase one component)
    - If P=2 and C=1, V=1 (Two phase one component)
    - If P=1 and C=2, V=3 (One phase two component)

State Equation

- State Equation for a one component system:

$$f(P,v,T)=0 \qquad\qquad P=P(v,T)$$

- Examples
  - Ideal Gas Equation:

$$P=\rho\ R\ T$$

  - Ideal Liquid Equation:

$$\rho=cons.$$

Real Gases

- Ideal gas approximation fails at high pressures/low temperatures
  - Volume of the gas molecules become non trivial
  - Attraction/repulsion forces between molecules become significant
- Real gas. Compressibility factor (read *z* from charts)

$$z \equiv \frac{P}{\rho R T} = \frac{P V_m}{R_u T}$$

$V_m : Molar\ Volume$

- Equation of State (EOS) for real gases (Cubic equations)
  - Van der Waals

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = R_u T$$

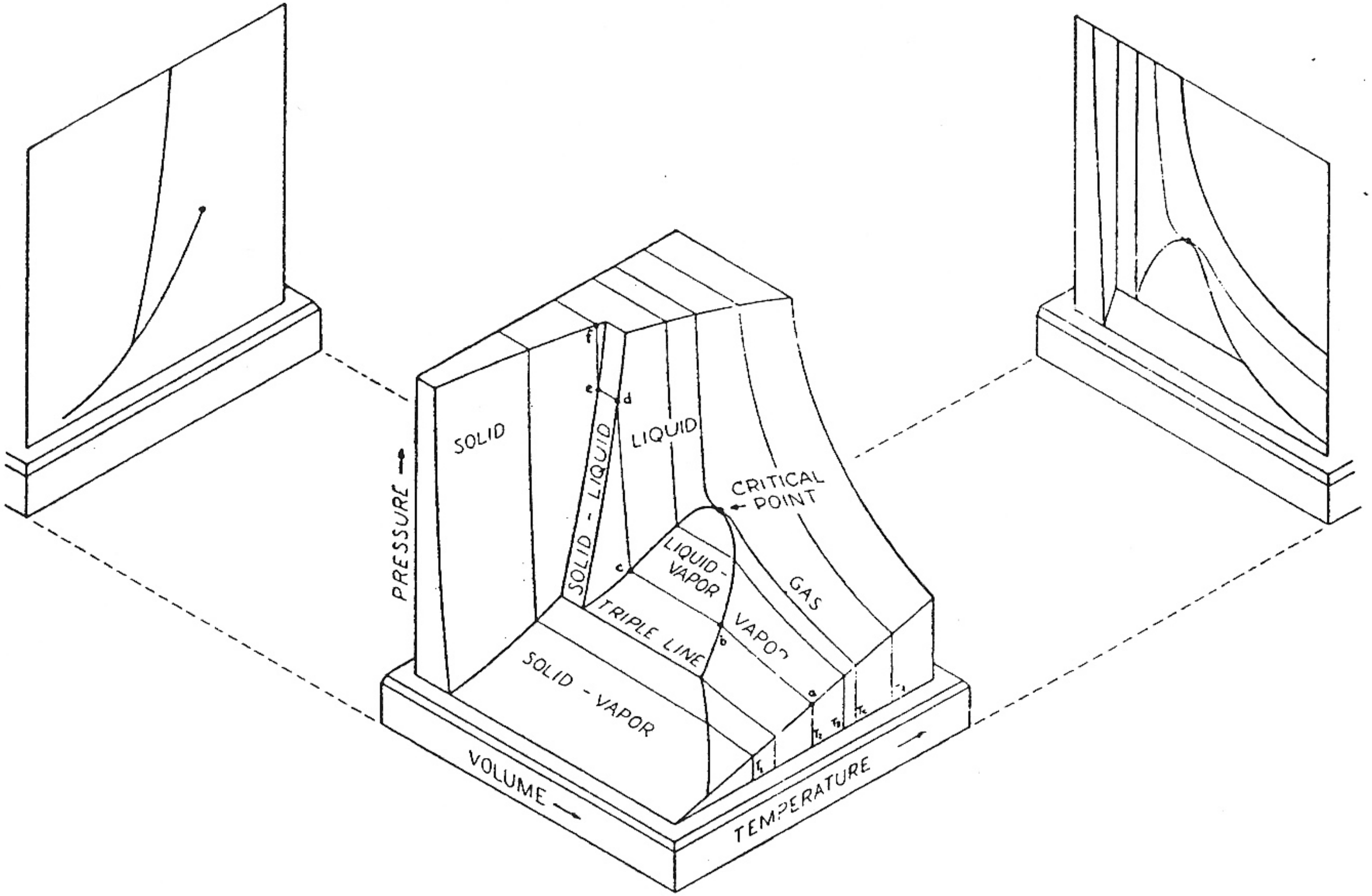
  - Redlich-Kwong EOS

$$\left(P + \frac{a}{T^{0.5} V_m (V_m - b)}\right)(V_m - b) = R_u T \qquad a = \frac{0.42748 R^2 T_c^{2.5}}{P_c} \qquad b = \frac{0.0866 R T_c}{P_c} \qquad z_c = \frac{P_c V_m}{R_u T_c} = \frac{1}{3}$$

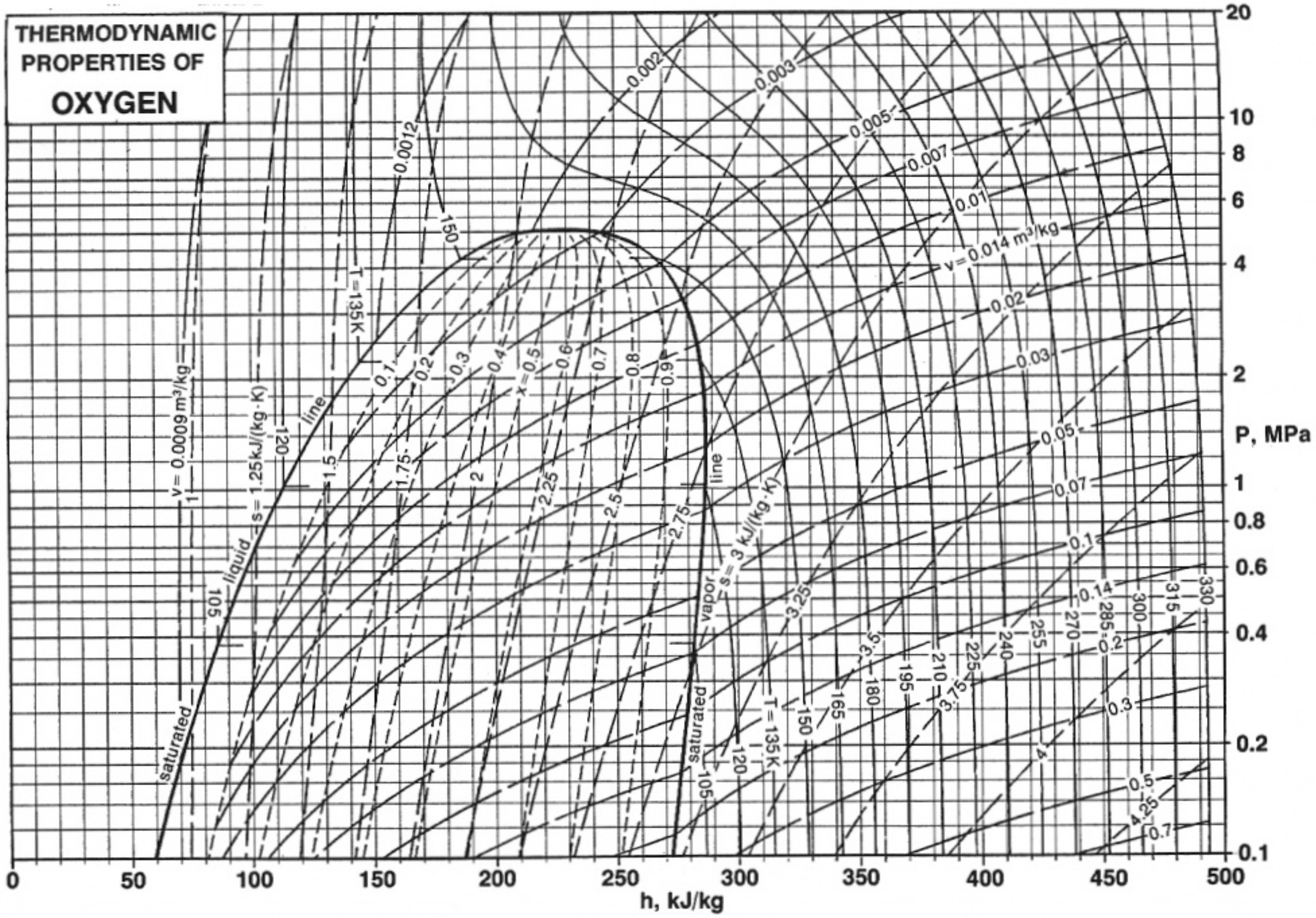
  - Peng-Robinson EOS

$$P = \frac{R_u T}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)}$$

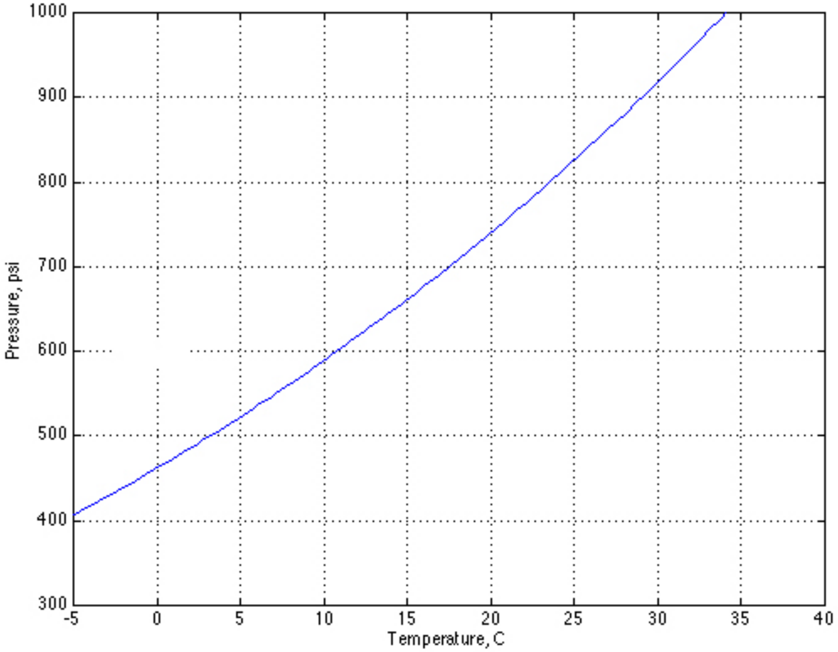
P-V-T Diagram of a Single Component Substance

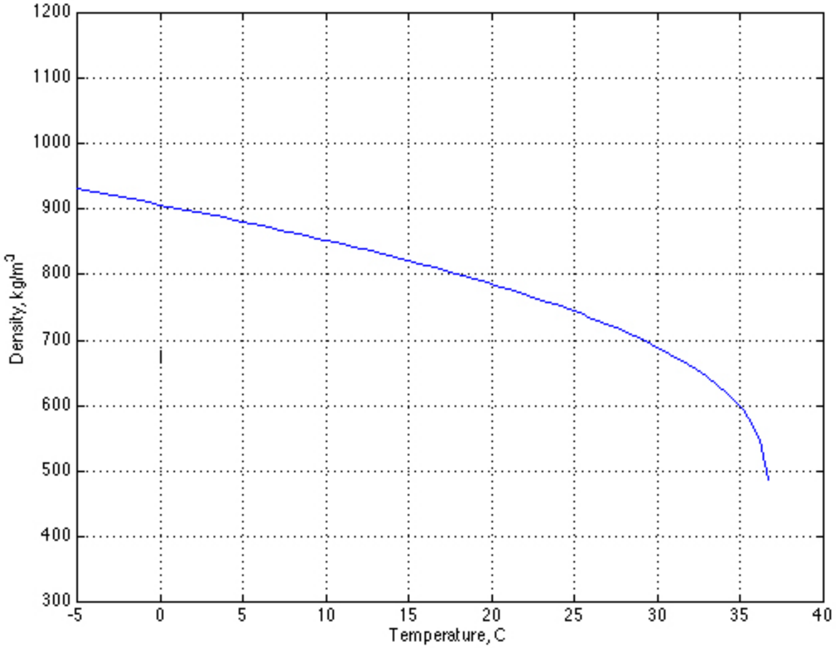


P-h Diagram Molecular Oxygen

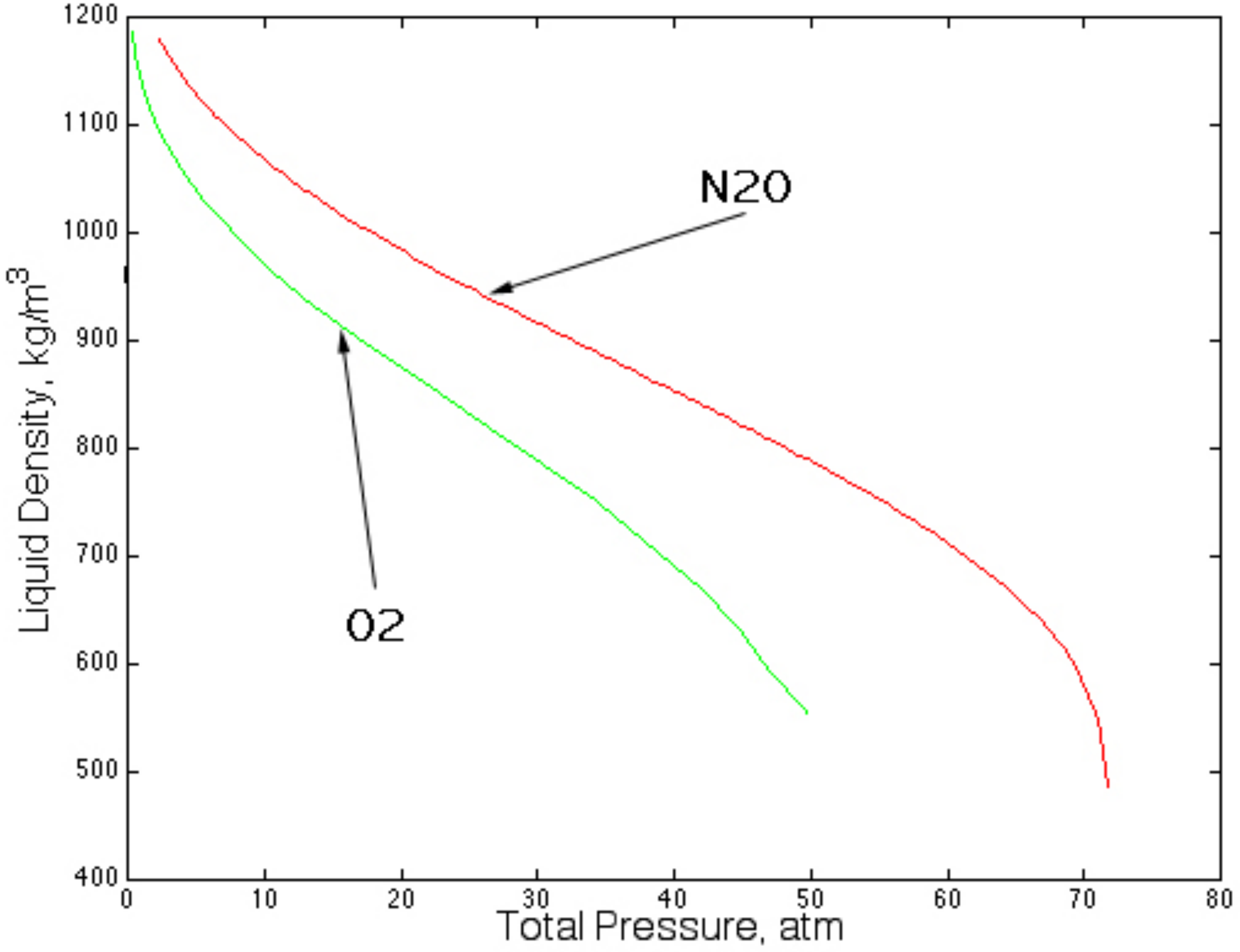


Saturation Pressure and Density Plots for N_2O





Saturation Pressure vs Saturation Density for Popular Oxidizers



Specific Heats

- Specific heats are defined as

$$c_p = \left.\frac{\partial h}{\partial T}\right|_P \qquad c_v = \left.\frac{\partial e}{\partial T}\right|_v$$

c_p : *Specific Heat @ Cons. Pressure*
c_v : *Specific Heat @ Cons. Volume*
γ : *Ratio of Specific Heats*

- For an ideal gas $h = h(T)$ $e = e(T)$

$$c_p = \frac{dh}{dT} \qquad c_v = \frac{de}{dT} \qquad c_p - c_v = R \qquad \gamma = \frac{c_p}{c_v}$$

- For a calorically perfect gas both specific heats are constant

$$c_p = \frac{N+2}{2} R \qquad c_v = \frac{N}{2} R$$

- *N* is the internal degrees of freedom (fully excited)

Specific Heats

- Monotonic gas: N=3 (3 translational DoF)
- Diatomic gas
  - Vibrational modes NOT excited: N=5 (+2 rotational DoF)
  - Vibrational modes fully excited: N=7 (+2 vibrational DoF)
  - For intermediate temperatures $(c_v)_{vib} = R\left(\frac{\Theta_v}{T}\right)^2 \frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T}-1\right)^2}$

$$\Theta_v \equiv \frac{h\nu}{k} = \text{Characteristic Temperature for Vibration}$$

$\nu = \text{Frequency}$

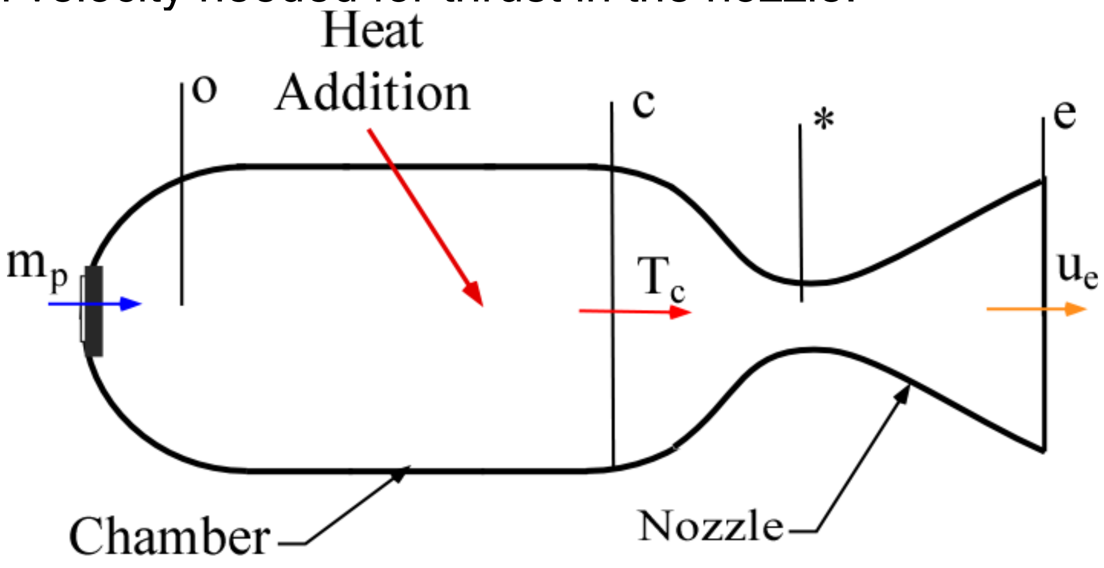
$\text{h : Planck's Cons.}$

  - Data for diatomic molecules

Characteristic Temperature	**N_2, K**	**O_2, K**
Rotational	2.9	2.1
Vibrational	3,390	2,270
Dissociation	113,000	59,500
Ionization	181,000	142,000

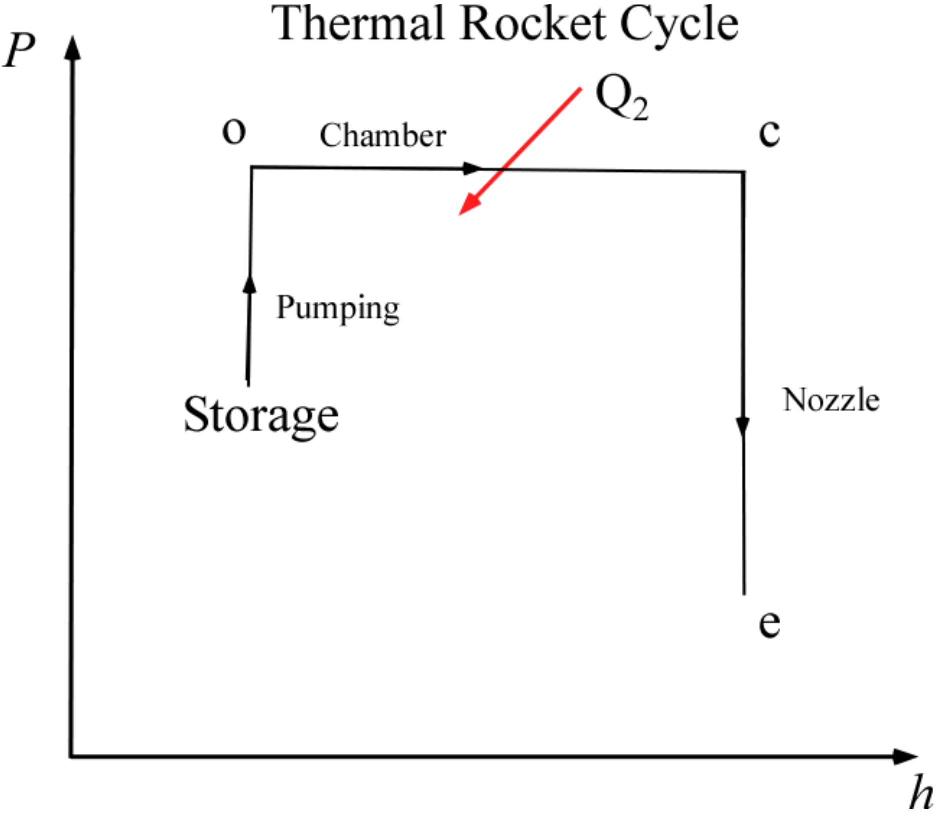
Thermal Rocket – General Concept

- In a thermal rocket the propellant molecules are thermalized by addition of heat in a chamber.
- This thermal energy (random motion of the molecules) is converted to the useful directional velocity needed for thrust in the nozzle.



- The heat source varies
  - Nuclear energy: Thermonuclear rockets
  - Chemical bond energy: Chemical rockets
  - Electric energy: Resistojets and Arcjets
  - Thermal energy of the stored propellant: Cold gas thrusters

Thermal Rocket – Thermodynamic Process



- Note that this is not really a cycle since the propellant never returns to its original state
- The velocity at the nozzle exit, u_e, can be estimated using the conservation of energy along a streamline

$$h_{tc} - h_e = \frac{1}{2} u_e^2$$

$$u_e = \sqrt{2\left(h_{tc} - h_e\right)}$$

- The maximum possible exit velocity (or Isp) is obtained for infinite expansion (he=0)

$$u_e = \sqrt{2\, h_{tc}}$$

- For calorically perfect gas

$$u_e = \sqrt{\frac{2\gamma}{\gamma - 1}} \sqrt{\frac{R_u T_{tc}}{Mw}}$$

- For monatomic gas:

$$u_e = 2.21 \sqrt{\frac{R_u T_{tc}}{Mw}}$$

Thermal Rocket – Velocities in Monatomic Gas

- Lets compare this maximum velocity to the other fundamental velocities that can be defined in a monatomic gas

$$\text{Maximum Directional Velocity:}\quad u_e = 2.21\sqrt{\frac{R_u T_{tc}}{Mw}}$$

$$\text{Isentropic Speed of Sound:}\quad a_s = 1.29\sqrt{\frac{R_u T_{tc}}{Mw}}$$

$$\text{Charactristic Velocity:}\quad c^* = 1.38\sqrt{\frac{R_u T_{tc}}{Mw}}$$

$$\text{Isothermal Speed of Sound:}\quad a_T = \sqrt{\frac{R_u T_{tc}}{Mw}}$$

$$\text{Most Probable Molecular Speed (Maxwellian Distribution):}\ C_{MP} = 1.41\sqrt{\frac{R_u T_{tc}}{Mw}}$$

$$\text{Average Molecular Speed (Maxwellian Distribution):}\quad \overline{C} = 1.60\sqrt{\frac{R_u T_{tc}}{Mw}}$$

$$\text{Square Averge Molecular Speed:}\quad \left(\overline{C^2}\right)^{1/2} = 1.72\sqrt{\frac{R_u T_{tc}}{Mw}}$$

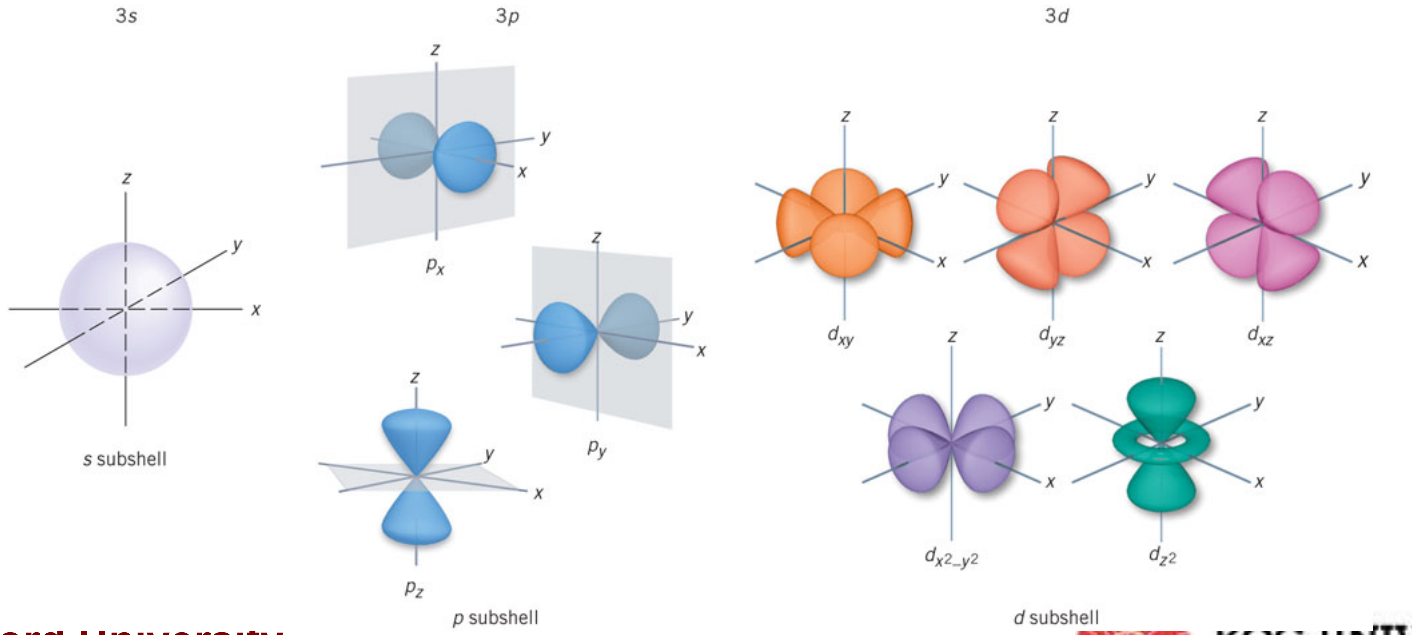
- Note that all of these speeds are of the same order (order of the average speed of the molecules in the gas)
- Similar results can be produced for other gamma values

Review of Chemistry

- Atomic Model: Negatively charged electrons are orbiting around the positively charged nucleus
- Schrodinger’s wave equation governs the size, number and shape of the orbitals

$$\left[-\frac{h^2}{8\pi^2 m_e}\nabla^2-\frac{Ze^2}{r}\right]\Psi=E\Psi$$

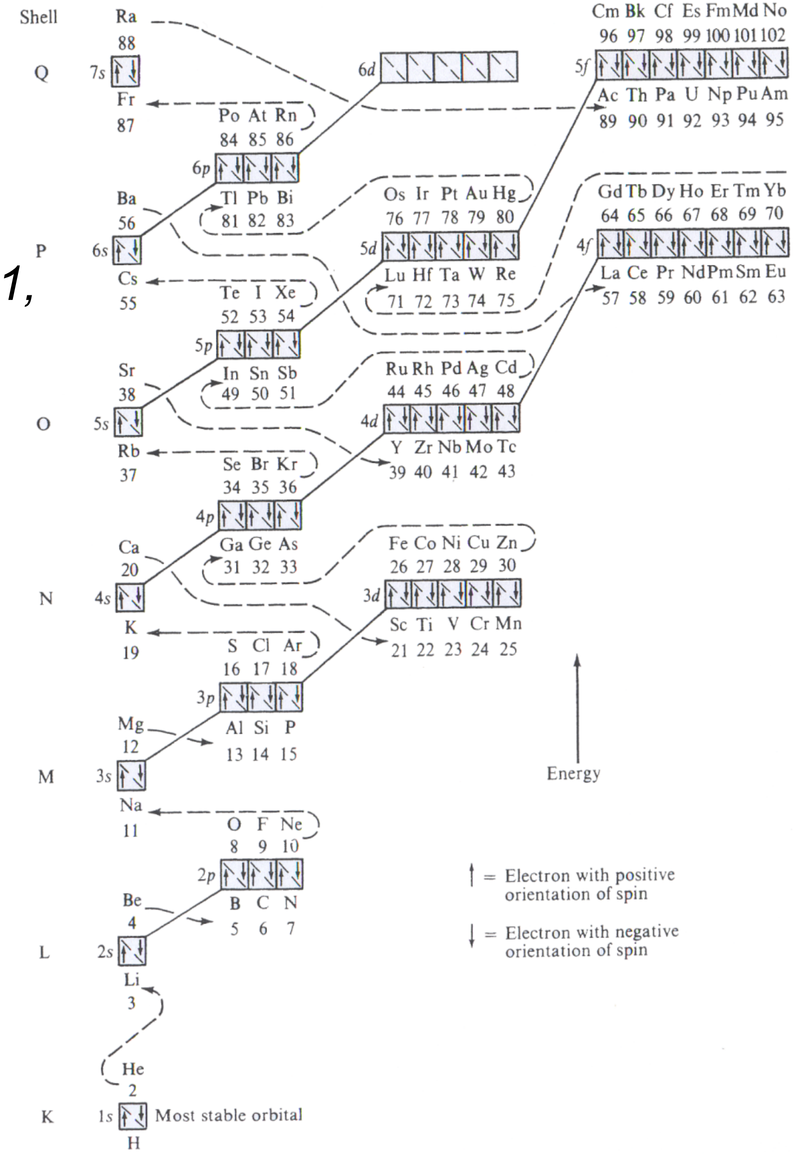
- Square norm of the wave function is a probability density function for the position or momentum of the electron
- Eigenvalue problem – Only discrete levels of energy is possible



Review of Chemistry – Energy Level Diagrams

Atomic Structure (Quantum Mechanics)

- Principal quantum number: *n=1, 2, 3 …*
  - *General energy level of the shell*
  - *n=1 (K), n=2 (L), n=3 (M),…*
- Angular momentum quantum number: *l=0, 1, …(n-1) [Orbital angular momentum]*
  - Determines the shape of the orbitals
  - *l=0 (s), l=1 (p), l=2, (d), …*
- Magnetic quantum number: m_l: *+l, +l-1,…0, …-(l-1), l*
  - *Determines the number of orbitals*
- Electron Spin quantum number, m_s
  - Each electron has: s=½ or -½ [Intrinsic angular momentum the electron]



Pauli Exclusion Principle:

“No two electrons in an atom may posses identical sets of values of the four quantum numbers *n, l,* $m_{l,,}$ m_s “

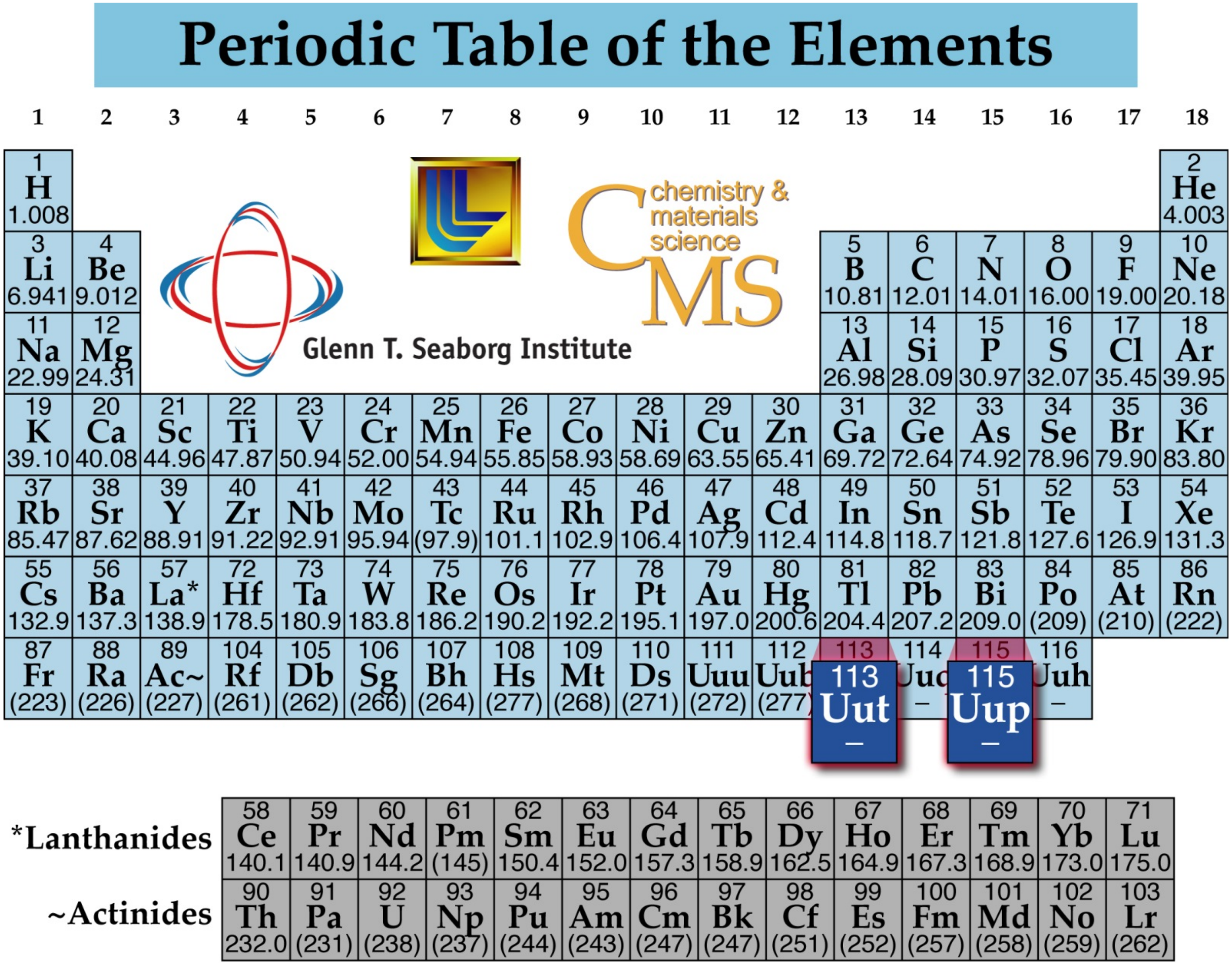
Review of Chemistry

n : *Principal Quantum Number*

- Quantum Mechanics Predicts:
  - Shells, subshells, orbitals
    - *n=1*: K shell (2 electrons)
      - 1s subshell (1 orbital): electrons
    - *n=2*: L shell (8 electrons)
      - 2s subshell (1 orbital): 2 electrons
      - 2p subshell (3 orbitals): 6 electrons
    - *n=3*: M shell
      - 3s subshell (1 orbital): 2 electrons
      - 3p subshell (3 orbitals): 6 electrons
      - 3d subshell: (5 orbitals): 10 electrons
- Argononic structures: Completely full shells (Noble elements: He, Ne, Ar …), Octets
- Valance electrons: Electrons in the shell that is not completely filled

Reference on Chemistry: Linus Pauling, “General Chemistry”

Periodic Table of Elements



Periodic Table of the Elements

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CMS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.9)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Uuu (272)	112 Uub (277)	113 Uut –	114 Uuq –	115 Uup –	116 Uuh –		

*Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
~Actinides	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

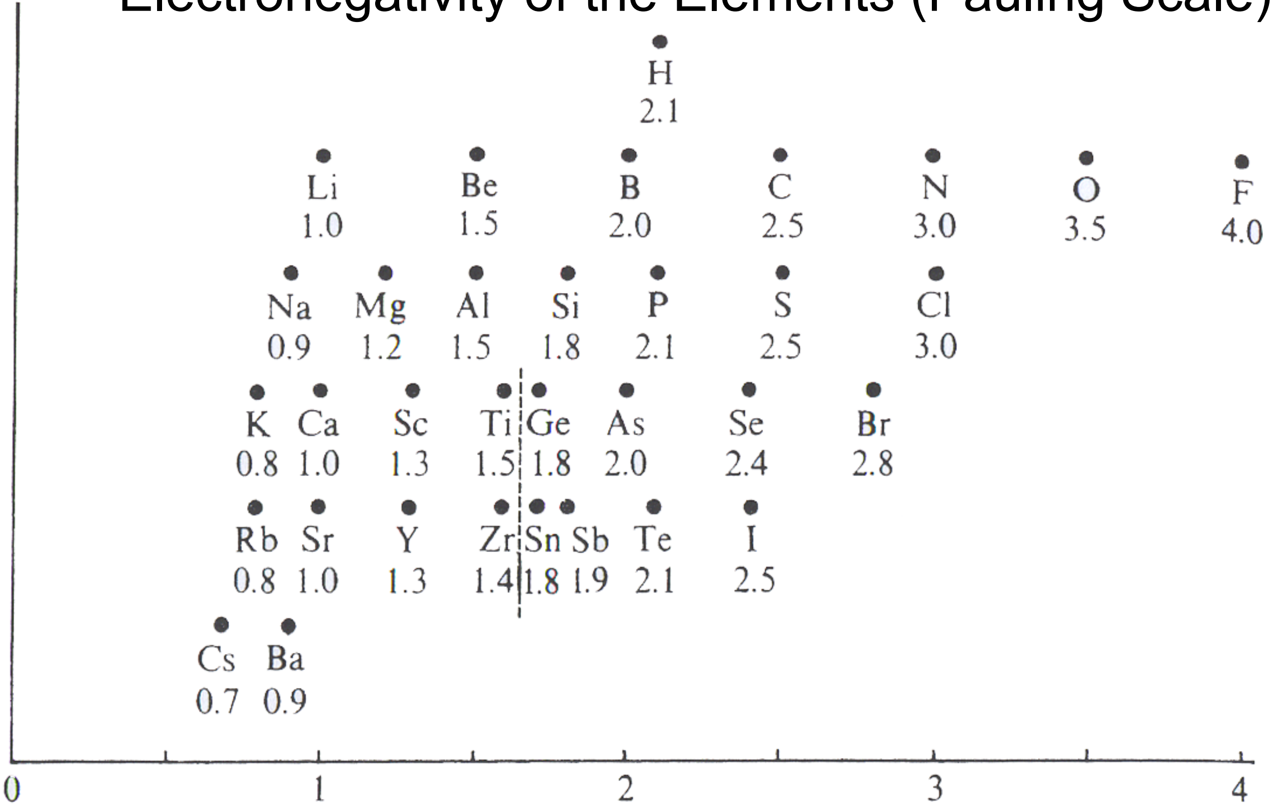
Review of Chemistry

- Elements in the same group have closely related physical and chemical properties (same number of valance electrons)
- Elements in the periods have their valance electrons in the same shell
- Left side of the periodic table : Metals (Fuels)
  - High electric and thermal conductivity, metallic luster, malleable, ductile
- Right side of the periodic table : Nonmetals (Oxidizers)
- Metalloids in the middle: B, Si, Ge, As
- Chemical Bonds:
  - Octet rule: Filled shell rule
    - Share or gain electrons to fill their shells to the Argononic structures
  - Covalent Bonds: Share pairs of electrons (H-C)
  - Ionic Bonds: Take or give electrons ($Li^{+}Cl^{-}$)
- Electronegativity: Affinity of an atom to an electron
  - The difference in electronegativity determines the covalent/ionic nature of the bond (Upper right highly electronegative, lower left poorly electronegative)
- Strained bonds (C3H6, C2H2) and Resonance Structures (N2O)

$$N\equiv\overset{+}{N}-O^{-} \longleftrightarrow {}^{-}N=\overset{+}{N}=O$$

Review of Chemistry – Electronegativity of the Elements

Electronegativity of the Elements (Pauling Scale)



Allred-Rochow Scale Electronegativity Coefficients: $\chi = \frac{3590\left(Z_{eff} - 0.35\right)}{r_{\text{cov}}^2} + 0.744$

Z_{eff} :Effective Atomic Number $\qquad r_{\text{cov}}$:Covelent Radius

Review of Chemistry – Electronegativity and Bonding

Influence of Electronegativity on Chemical Bonding