

AA103

Chemical Combustion

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April 23, 2019

Quick Review

$$c^* = \frac{P_t A^*}{\dot{m}} = \sqrt{\frac{R_u T_t}{\gamma M_w}} \left[\frac{\gamma + 1}{2} \right]^{\frac{\gamma+1}{2(\gamma-1)}}$$

$$C_f = \frac{T}{P_t A^*} = \frac{\left(\frac{\gamma+1}{2} \right)^{\frac{\gamma+1}{-2(\gamma-1)}}}{M_e \sqrt{1 + \frac{\gamma-1}{2} M_e^2}} \left[\gamma M_e^2 + 1 - \frac{P_0}{P_e} \right]$$

$$C = \frac{T}{\dot{m}} = C_f c^*$$

$$= (P_e - P_0) \frac{A_e}{\dot{m}} + \sqrt{\frac{2\gamma}{\gamma-1} \frac{R_u T_t}{M_w} \left[1 - \left(\frac{P_e}{P_t} \right)^{(\gamma-1)/\gamma} \right]}$$

C , c^* and C_f are very useful parameters but we need to learn more to compute them for chemical rockets

Assumes: Ideal gas, constant specific heat, isentropic, non-reacting flow

In chemical rockets, T and C depend on many 2nd order factors and are thus **hard to measure and predict**

- ▶ Prediction requires to T_t and M_w

c^* useful because:

- ▶ Measurable in experiment
- ▶ Dependent on propellant combustion and chamber conditions only

C_f useful because:

- ▶ Depends *almost* exclusively on nozzle performance & pressures

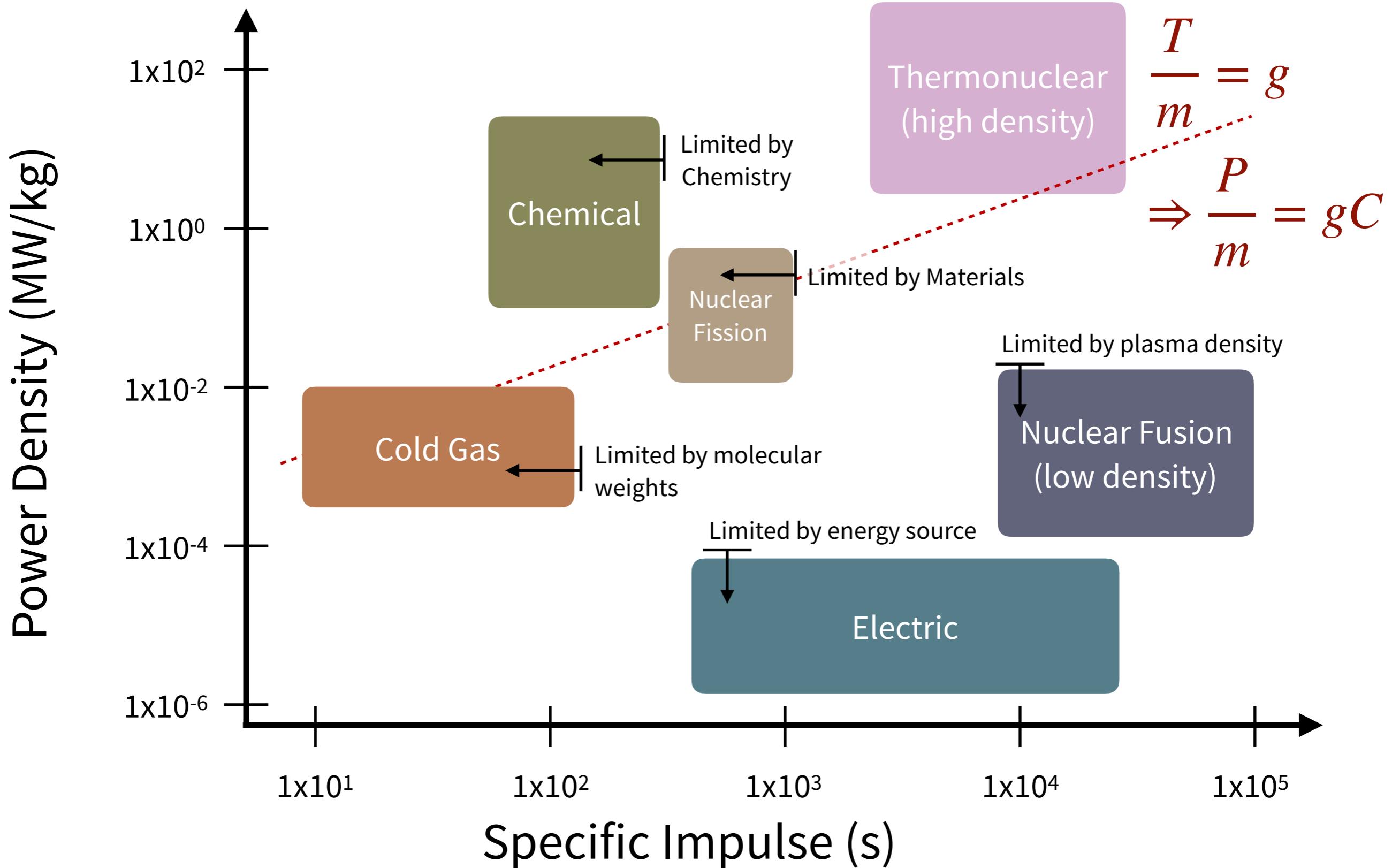
Why Chemical Combustion?

Technology	Isp (s)	Exhaust Velocity (m/s)
Nuclear Fusion	10,000 - 50,000+	98,000 - 490,000+
Electric Propulsion	1,000 - 10,000	9,800 - 98,000
Nuclear Thermal (fission)	600 - 1,000	5,900 - 9,800
Beamed Thermal (microwave / laser)	600 - 1,000	5,900 - 9,800
Bipropellant Chemical Propulsion	200 - 500	2,000 - 4,900
Monopropellant Chemical Propulsion	100 - 250	980 - 2,450
Cold Gas Propulsion	10 - 120	100 - 1,150

Energy Source	Power Density	Energy Density
SSME H ₂ /O ₂	2.8 MW/kg	19.4 MJ/kg
Nuclear Fission ¹	0.08 MW/kg	68.9 MJ/kg
Lilon Battery	3×10^{-4} MW/kg	0.7 MJ/kg
Triple-junction Solar Panel[1]	7×10^{-5} MW/kg	unlimited

¹NERVA flight-weight fission reactor

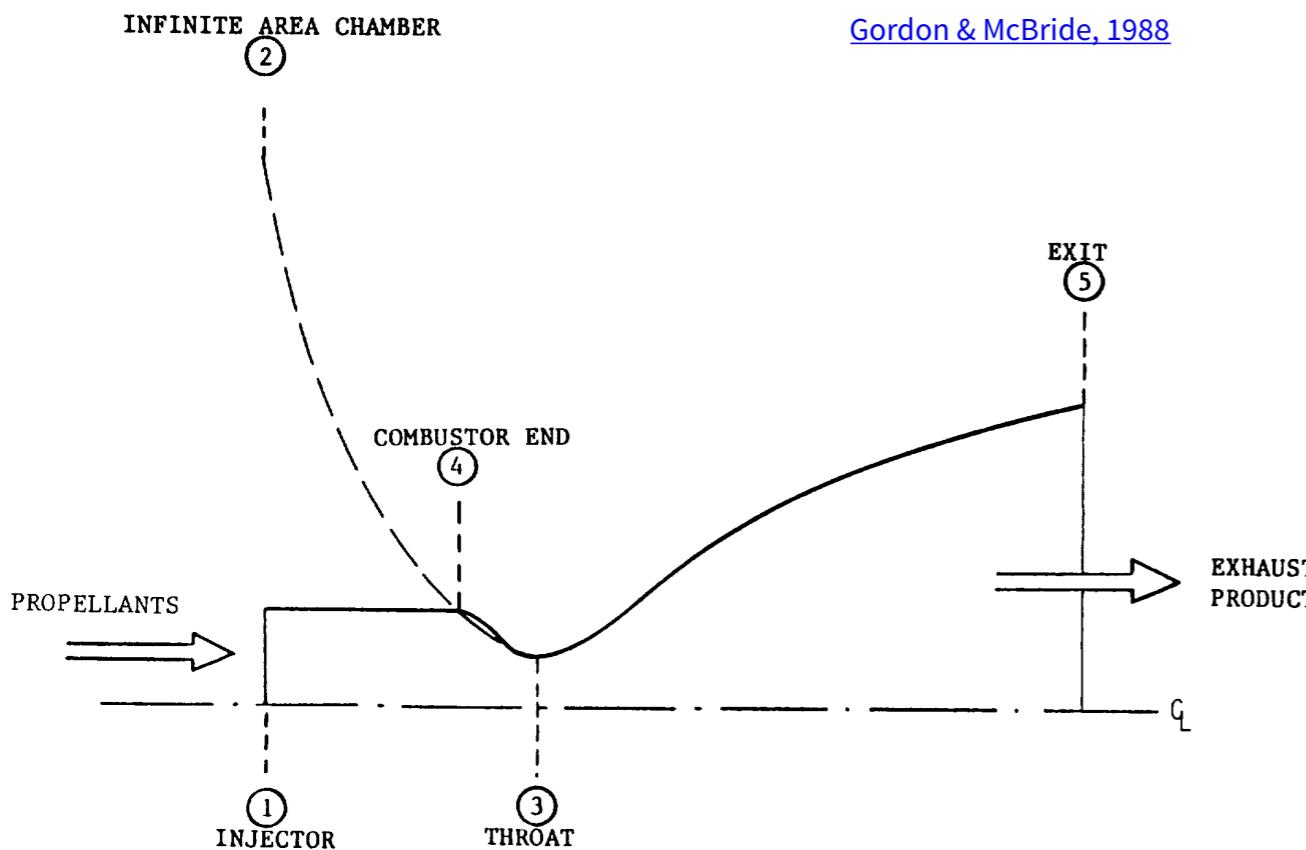
Propulsion Energy & Power Density



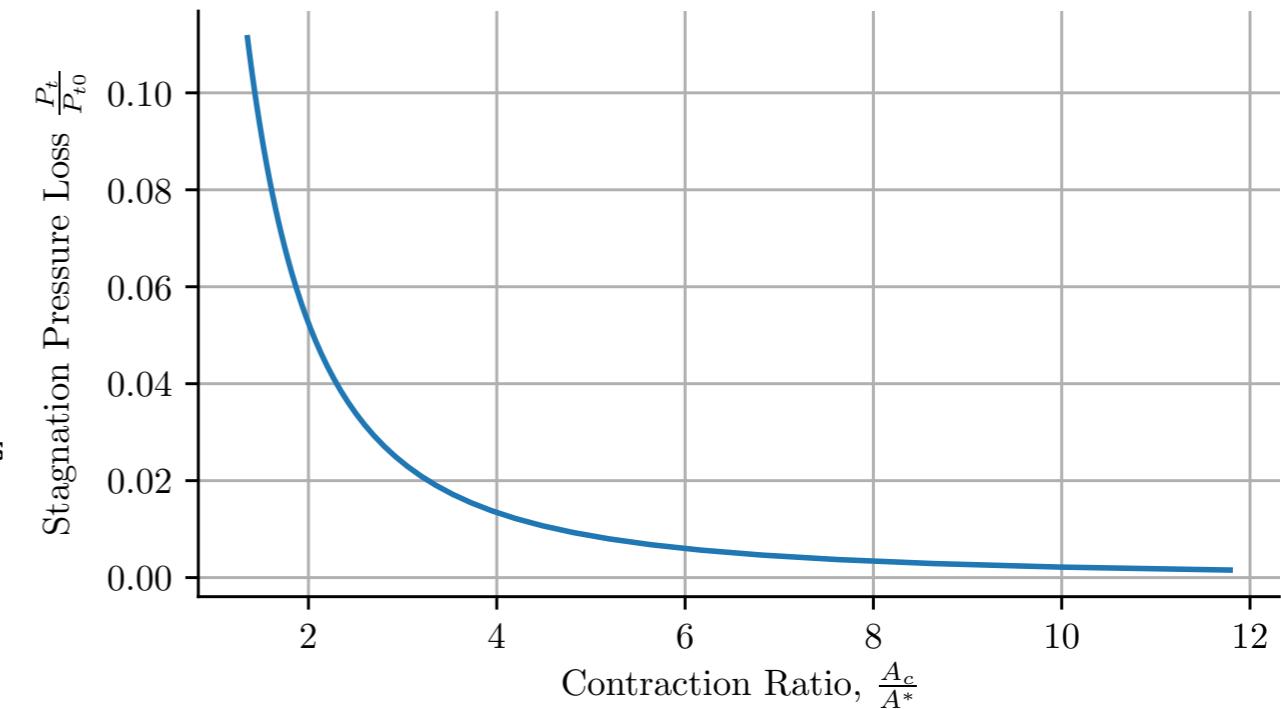
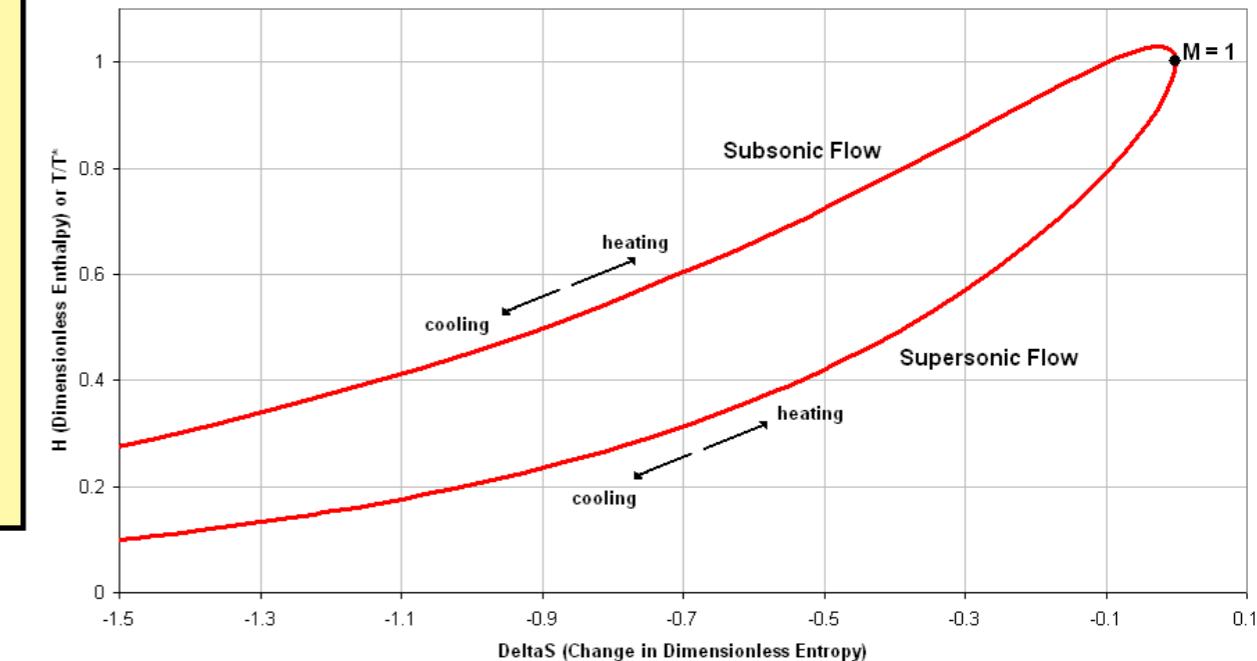
Finite Chamber Area

Heat addition in non-zero Mach-number flow causes irreversible stagnation pressure loss (Rayleigh Flow)

$$\frac{P_t}{P_{t0}} = \frac{1}{1 + \gamma M^2} \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}}$$



Rayleigh Line Plot (H-DeltaS Diagram)
Specific Heat Ratio = 1.4



Real Rocket Combustion is Complex

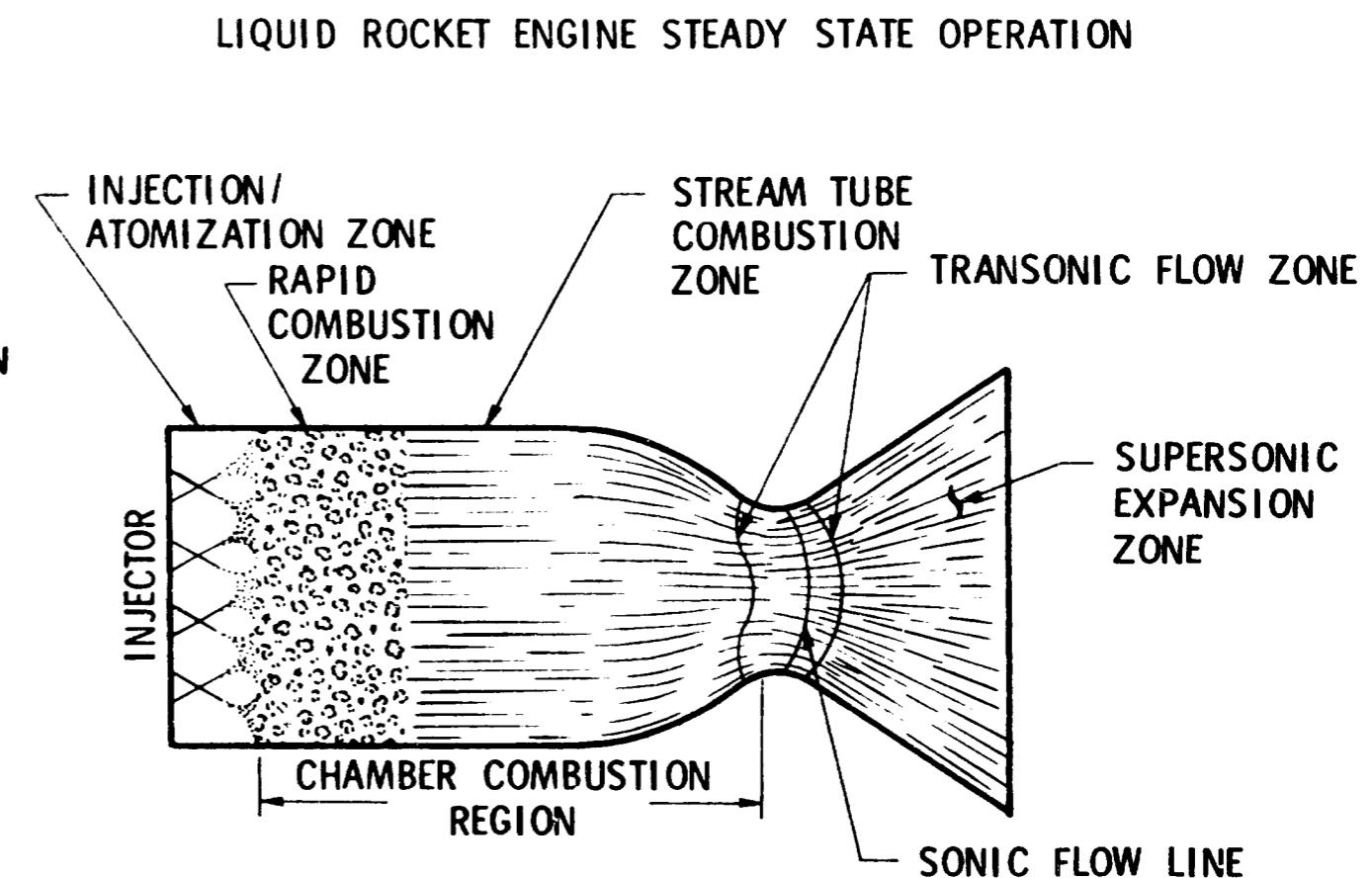
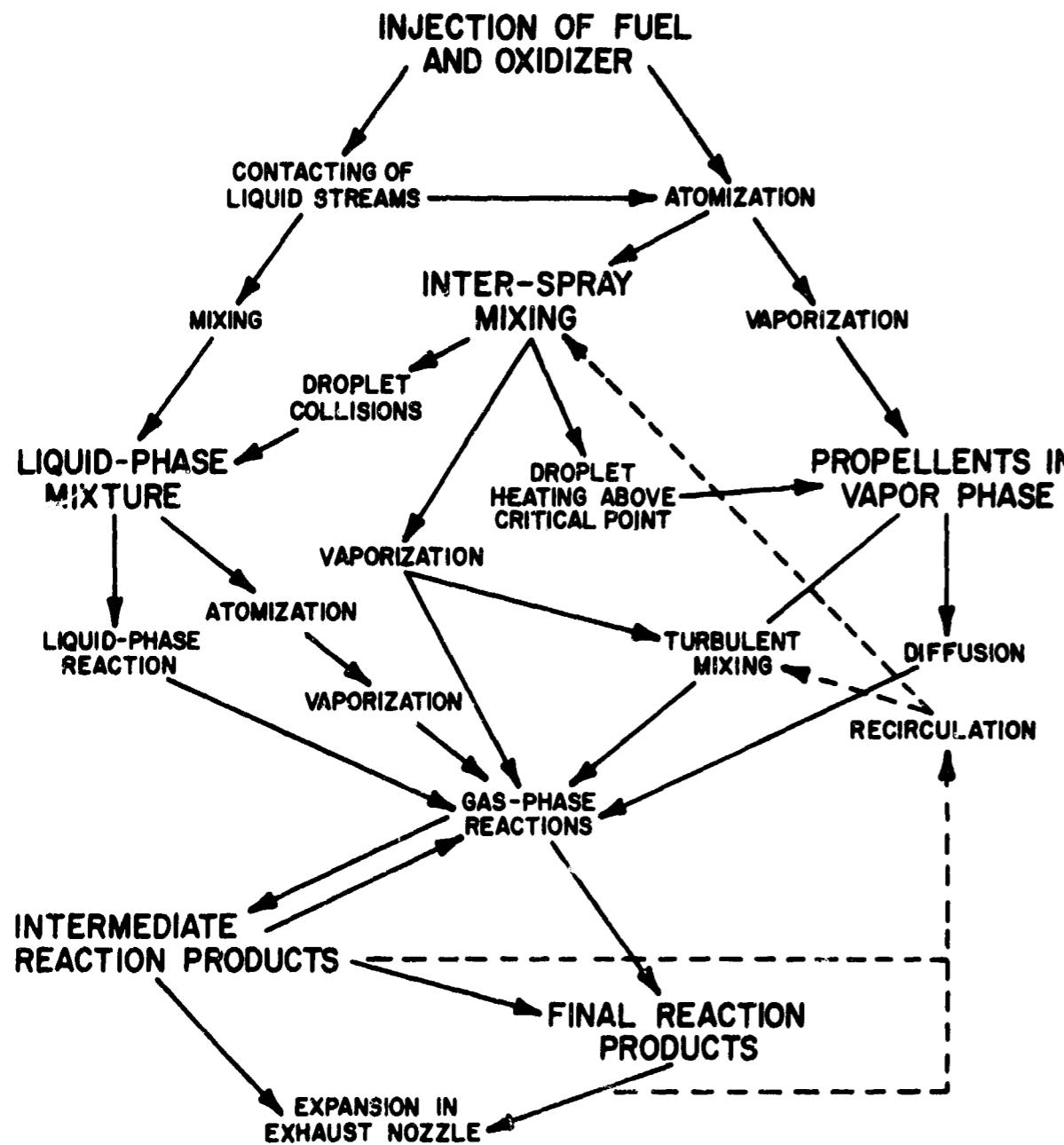
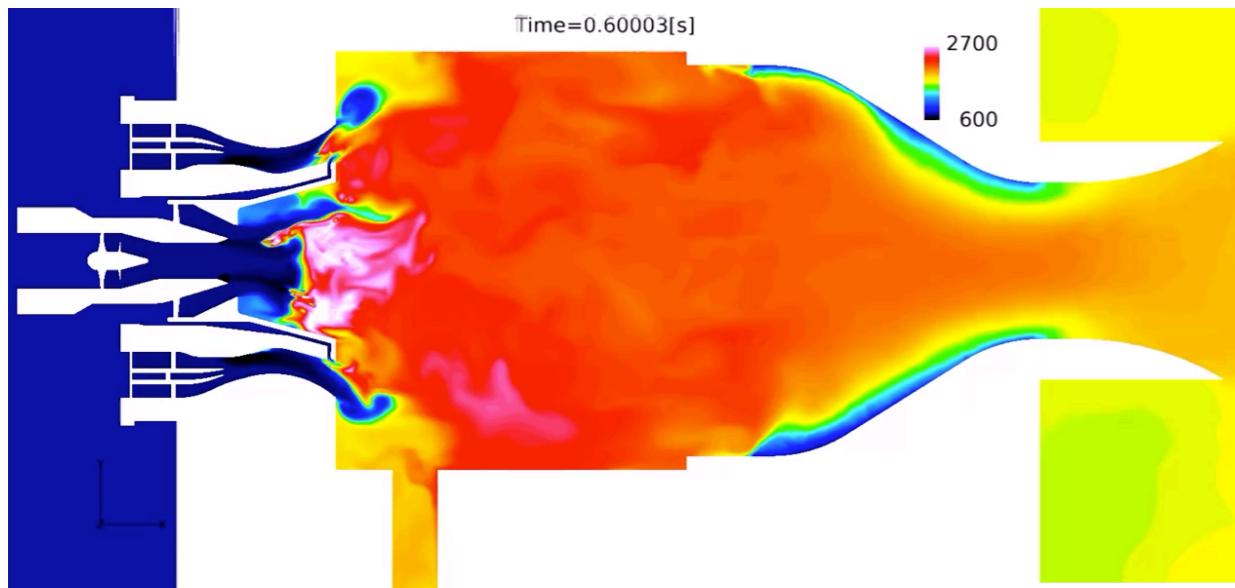
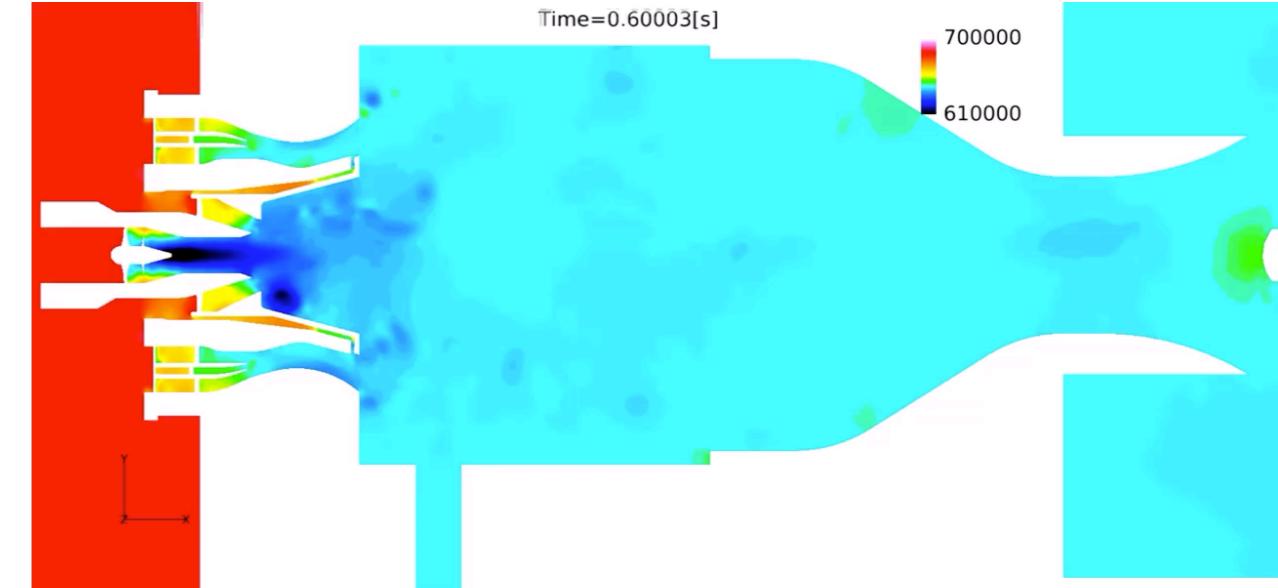


Figure 1. Schematic Representation of Liquid Propellant Rocket Combustion Processes

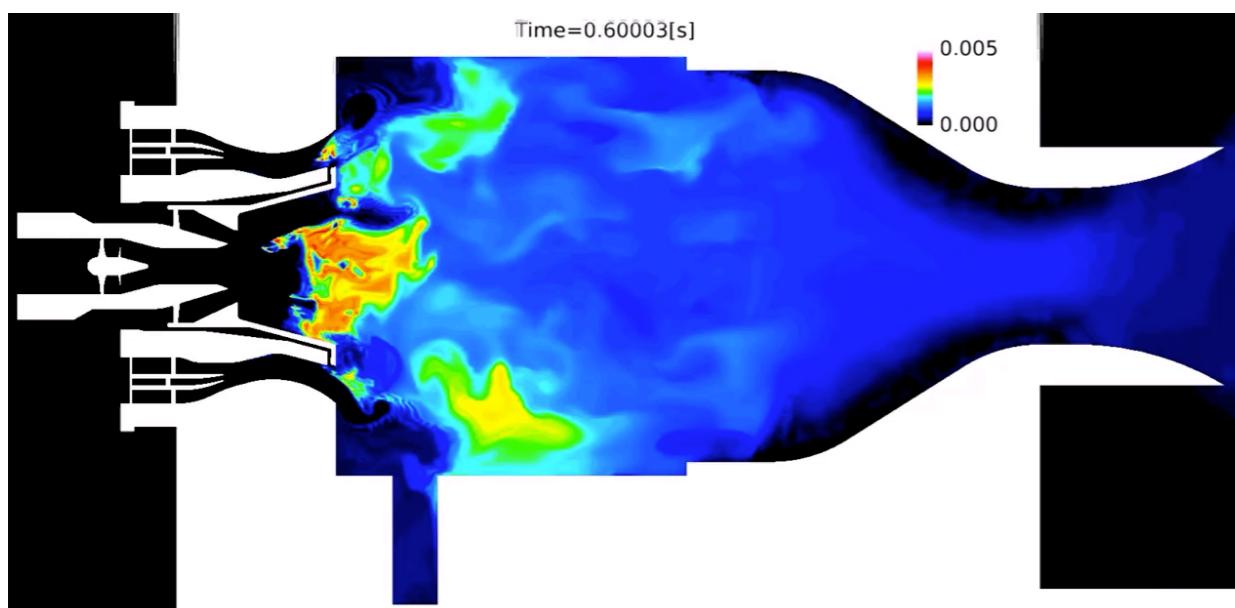
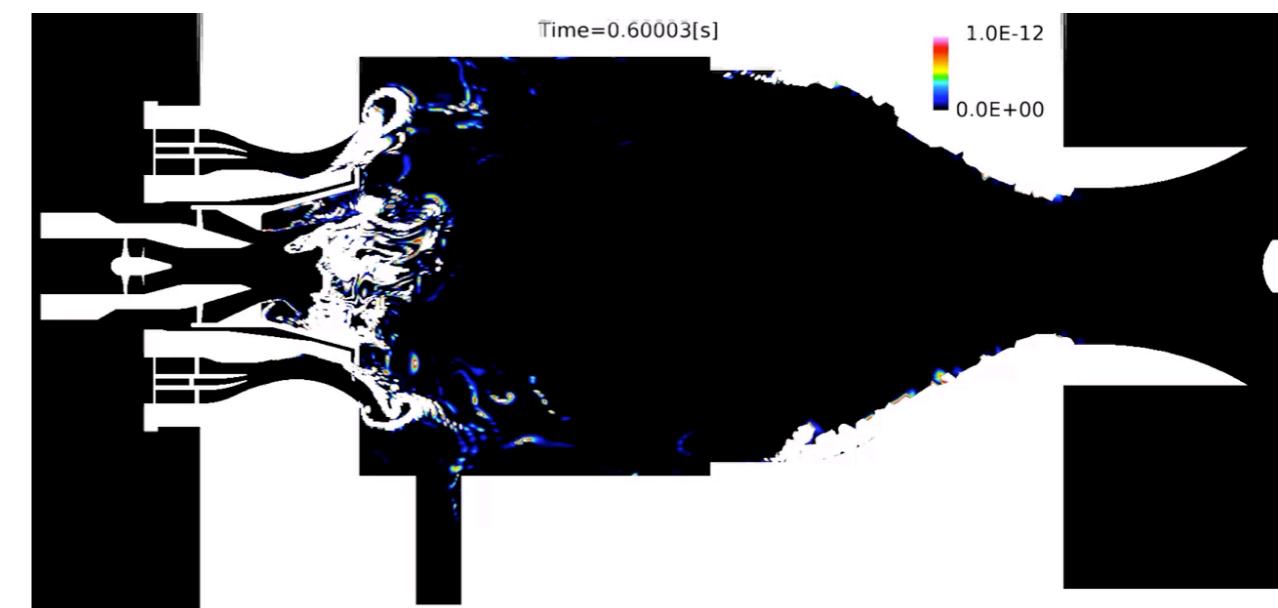
Real Rocket Combustion is Complex



Temperature



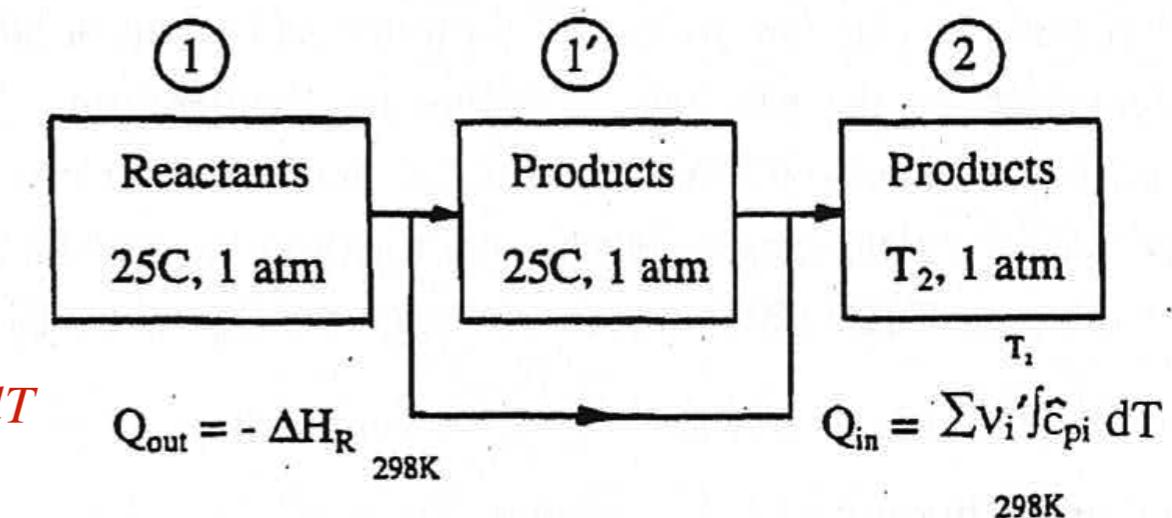
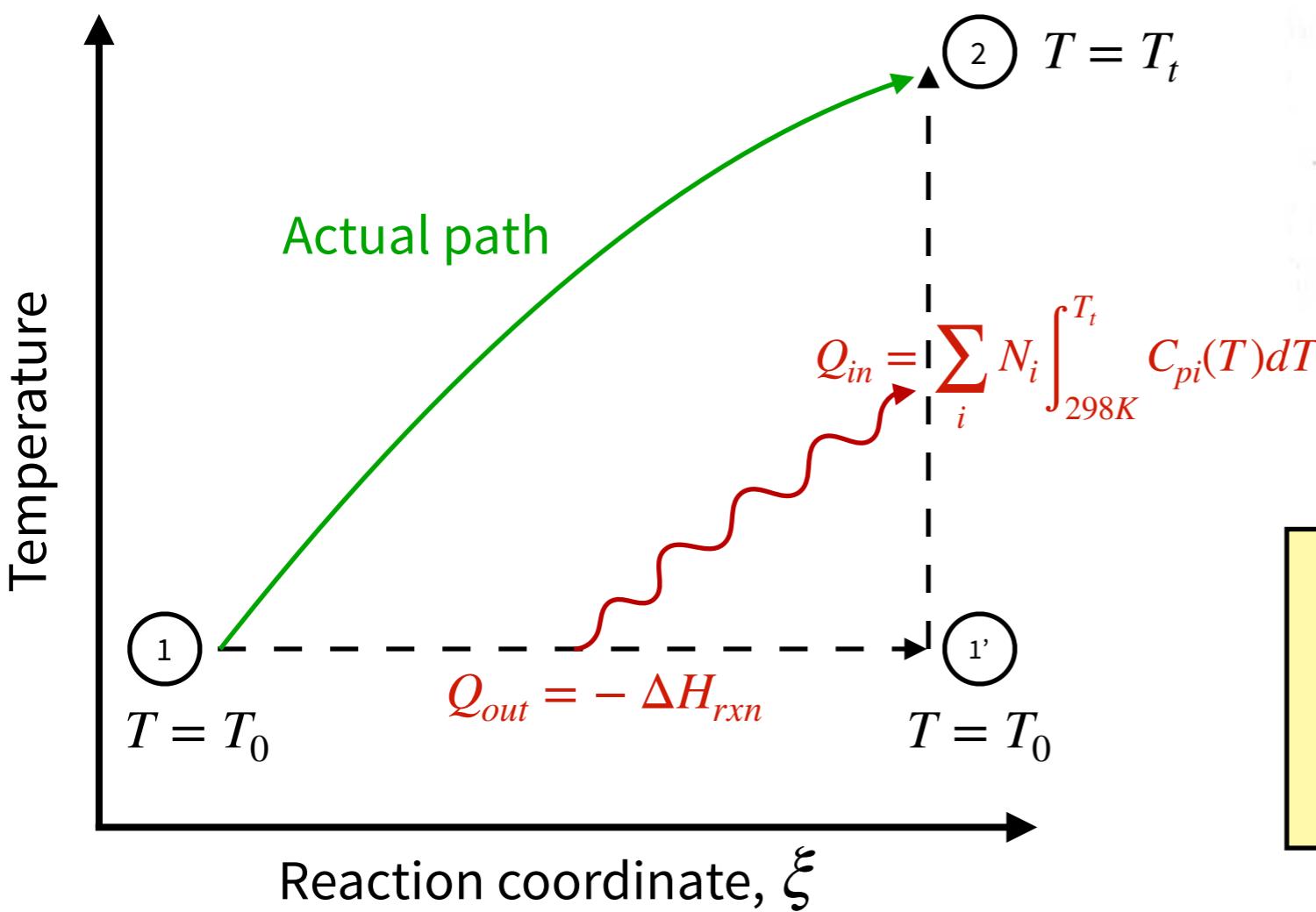
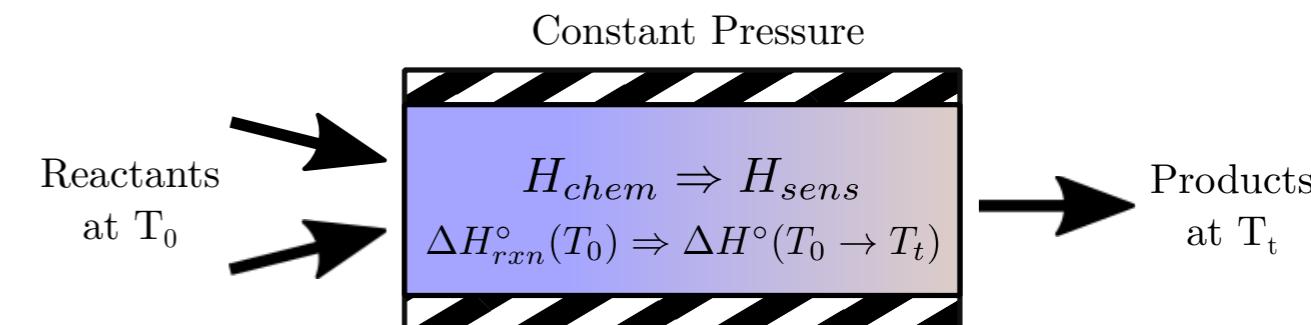
Pressure

 X_{OH}  X_{CH}

Adiabatic Combustion

First step towards reasonable model for T_t and M_w

- ❖ Constant pressure
- ❖ Thermodynamic equilibrium chemistry
- ❖ Ideal gas but variable specific heats

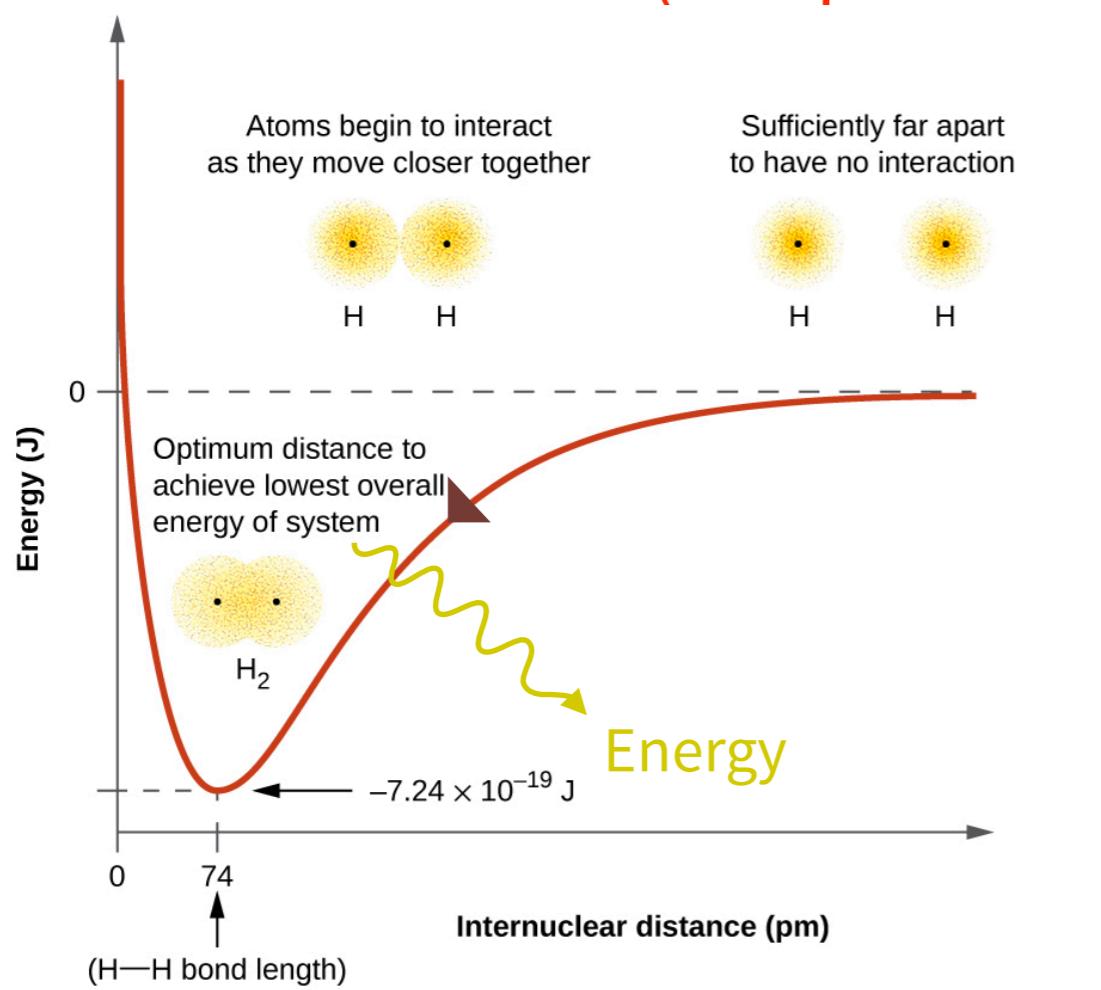


Adiabatic combustion is modeled as a three-step process

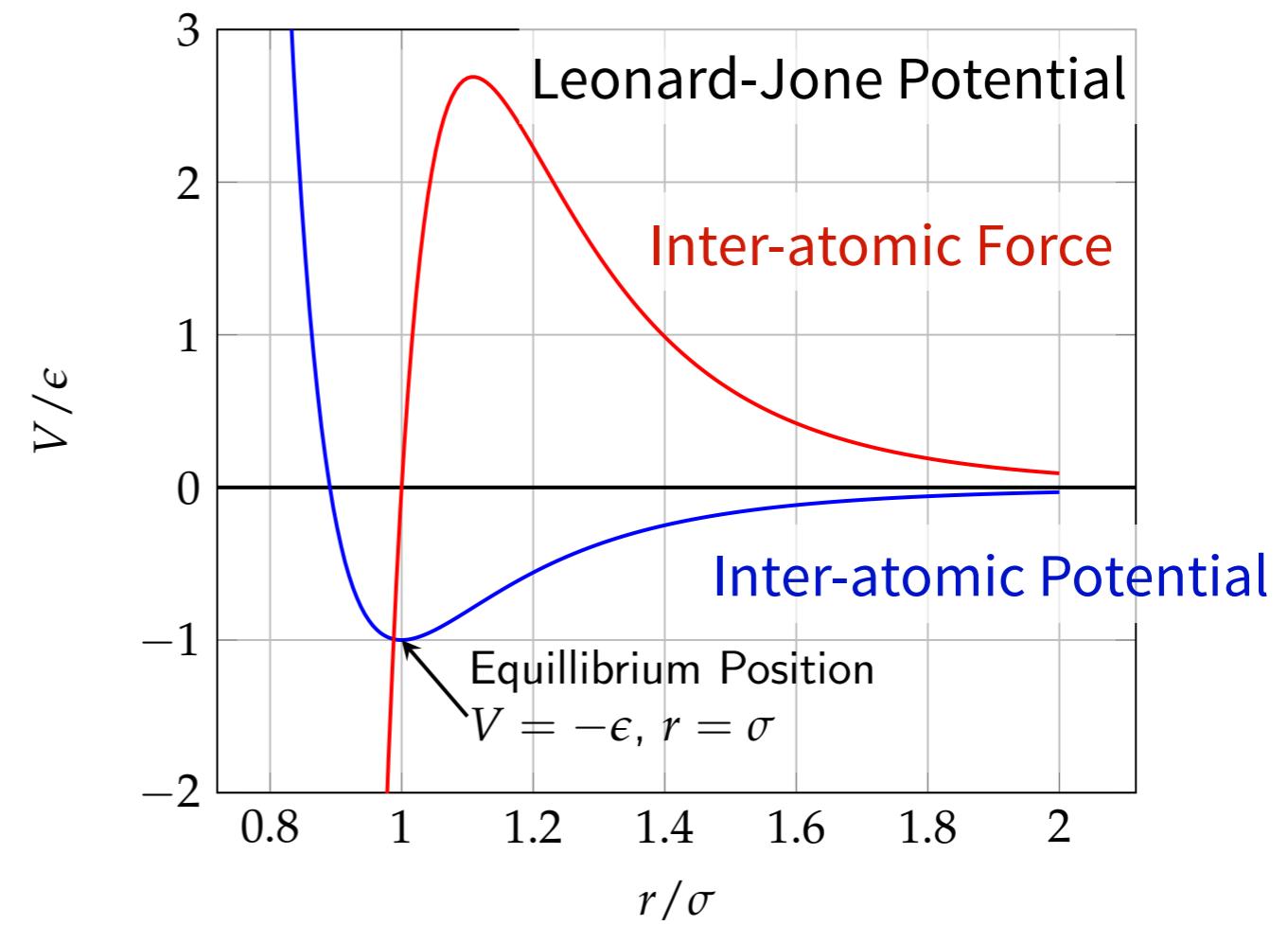
Origins of Chemical Energy

$$E = E_{chemical} + E_{sensible}$$

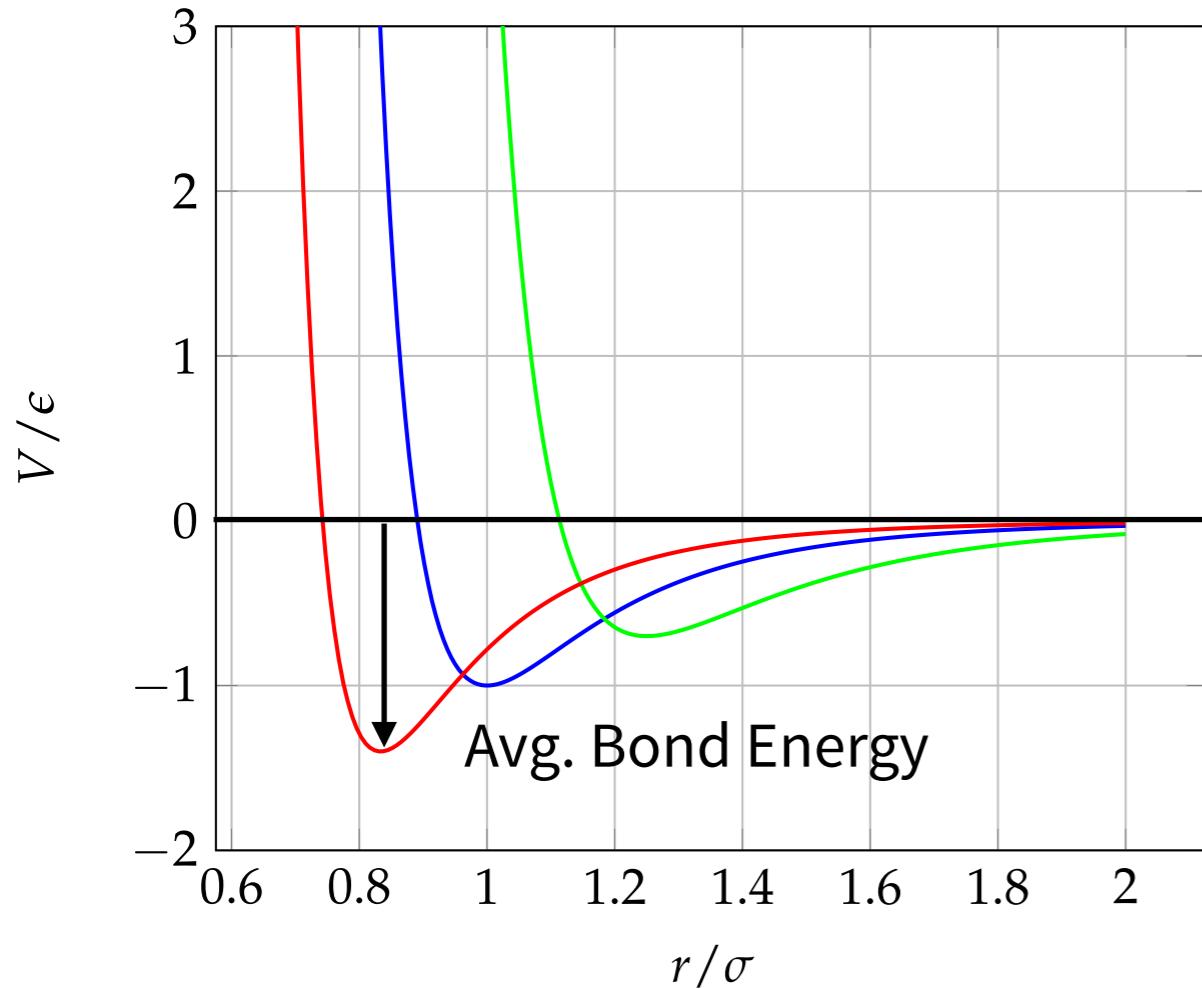
The diagram illustrates the decomposition of total energy into its components. A blue bracket under the term $E_{chemical}$ indicates that it corresponds to Potential Energy. A red bracket under the term $E_{sensible}$ indicates that it corresponds to Kinetic Energy (Temperature).



Total energy consists of sensible (observable) and latent (invisible) energy. Chemical energy is one form of latent energy



Bond Energy



Real bonds have different lengths and energies

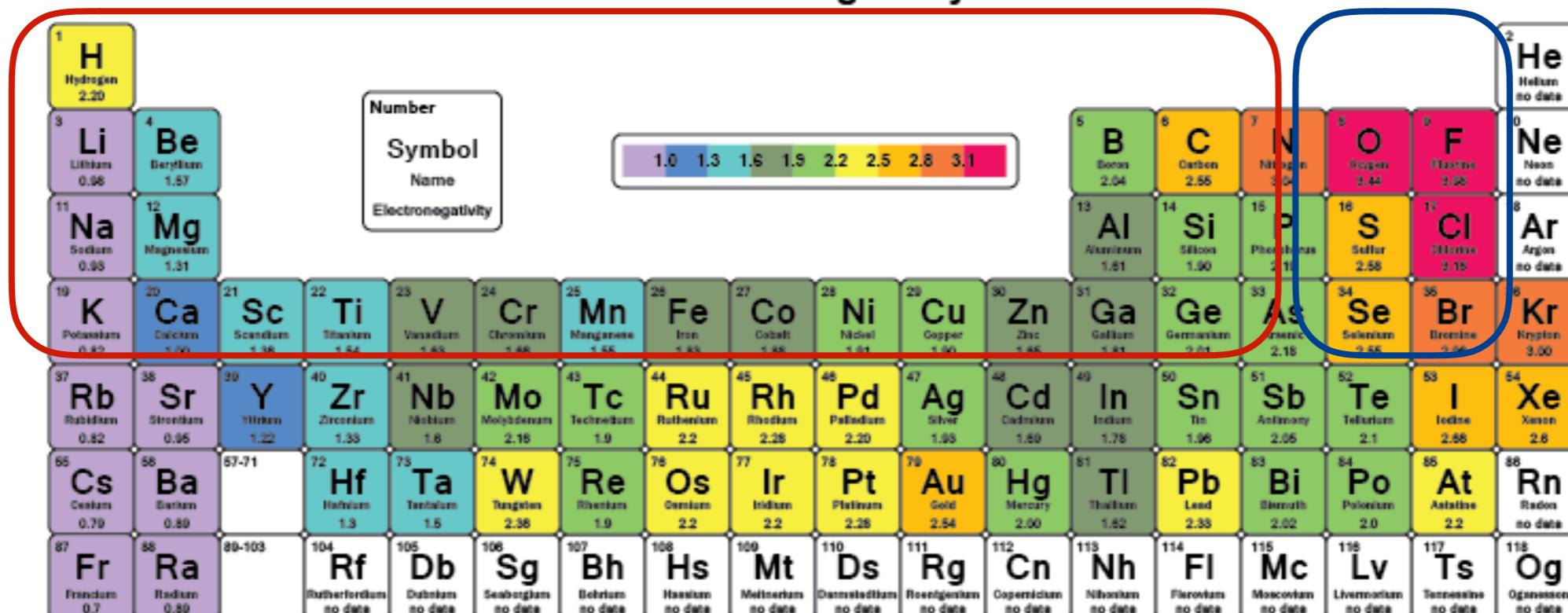
Bond	Avg. Energy (kJ/mol)	Avg. Length (Å)
H–H	432	0.74
N–N	167	1.45
F–F	155	1.42
O–O	142	1.48
H–F	565	0.92
H–O	459	0.96
H–Cl	428	1.27
H–S	363	1.34
H–C	413	1.09
C–F	485	1.35
C–O	358	1.43
C–C	346	1.54
C=C	602	1.34
C≡C	835	1.20
N=N	418	1.25
N≡N	942	1.10
N=O	607	1.21
O=O	494	1.21
C=O	799	1.20
C≡O	1072	1.13

Electronegativity

“Fuels”

Periodic Table of the Elements
Electronegativity

“Oxidizers”



Lanthanide Series	67 La Lanthanum 1.10	68 Ce Cerium 1.12	59 Pr Praseodymium 1.13	60 Nd Neodymium 1.14	61 Pm Promethium 1.15	62 Sm Samarium 1.17	63 Eu Europium 1.2	64 Gd Gadolinium 1.2	65 Tb Terbium 1.22	66 Dy Dysprosium 1.23	67 Ho Holmium 1.24	68 Er Erbium 1.24	69 Tm Thulium 1.25	70 Yb Ytterbium 1.1	71 Lu Lutetium 1.27
Actinide Series	89 Ac Actinium 1.1	90 Th Thorium 1.3	91 Pa Protactinium 1.5	92 U Uranium 1.38	93 Np Neptunium 1.38	94 Pu Plutonium 1.28	95 Am Americium 1.3	96 Cm Curium 1.3	97 Bk Berkelium 1.3	98 Cf Californium 1.3	99 Es Einsteinium 1.3	100 Fm Fermium 1.3	101 Md Mendelevium 1.3	102 No Nobelium 1.3	103 Lr Lawrencium no data

In general larger difference in electronegativity corresponds with larger (more negative) bond energy

Nomenclature

Associated with formation reaction

$$\Delta_f$$

Standard state pressure

\circ

Mole number, mass

$$n_i, m_i$$

Mole fraction

$$X_i = \frac{n_i}{\sum_i n_i}$$

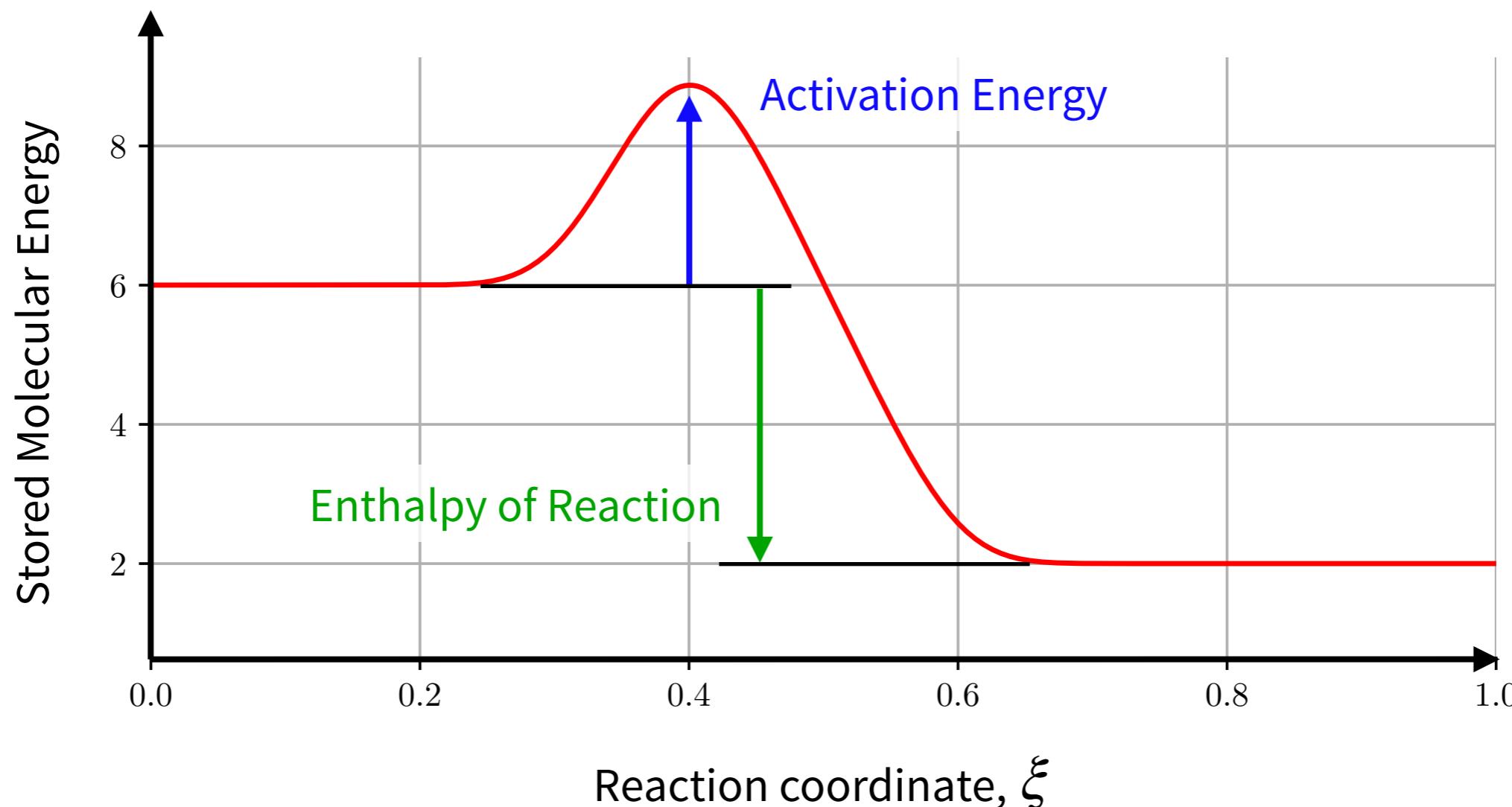
Extensive variable

$$H, U, V, S \dots$$

Intensive variable

$$h, u, v, s \dots$$

Standard Enthalpy (Heat) of Reaction



$$\Delta H_{rxn}^{\circ} = \sum_I n_i \Delta_f H_i^{\circ}(T_{ref})|_{product} - \sum_I n_i \Delta_f H_i^{\circ}(T_{ref})|_{reactant}$$

Standard/Reference States and Reference Species

- ▶ Most energetic variables have no meaning in an absolute sense - **need a reference against to measure**
 - ▶ We will use the [JANAF](#) / IUPAC (SATP) standard state of $P = 1\text{bar}$ ($1 \times 10^5 \text{ Pa}$) and reference temperature $T = 298.15\text{K}$
- ▶ In order to compare energies in a chemical reaction, also need to define a set of **reference species**
 - ▶ We will use the [JANAF](#) reference species which are generally the most stable single-element molecule (e.g. H_2 , O_2 , N_2)
- ▶ We must be able to compute properties of many substances away from the reference state. More on this later...

1st Law and Total Enthalpy

Enthalpy, like internal energy, is made up of sensible and latent components. Given a reference state and set of reference species the *total enthalpy* is

$$\begin{aligned} h_i^\circ(T) &= h_i^{chemical} + h_i^{sensible} \\ &= \Delta_f H_i^\circ(T_{ref}) + \Delta h_i^\circ(T) \\ &= \Delta_f H_i^\circ(T_{ref}) + \int_{T_{ref}}^T C_p(T) dT \end{aligned}$$

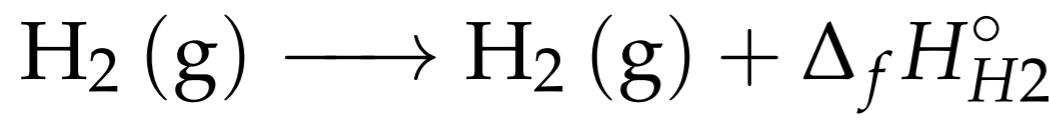
Note that we need to have defined the reference species for $\Delta_f H_i^\circ(T_{ref})$ to have any meaning!

$$\sum_I n_i h_i^\circ(T_{ref})|_{reactant} = \sum_I n_i h_i^\circ(T_t)|_{product}$$

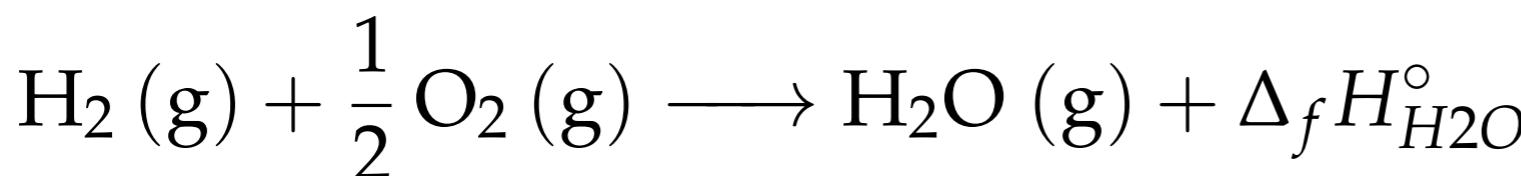
Formation reactions

$$\Delta H_{rxn}^\circ = \sum_I n_i \Delta_f H_i^\circ(T_{ref})|_{product} - \sum_I n_i \Delta_f H_i^\circ(T_{ref})|_{reactant}$$

We define a set of formation reactions to derive the reference state properties for species that are not reference species

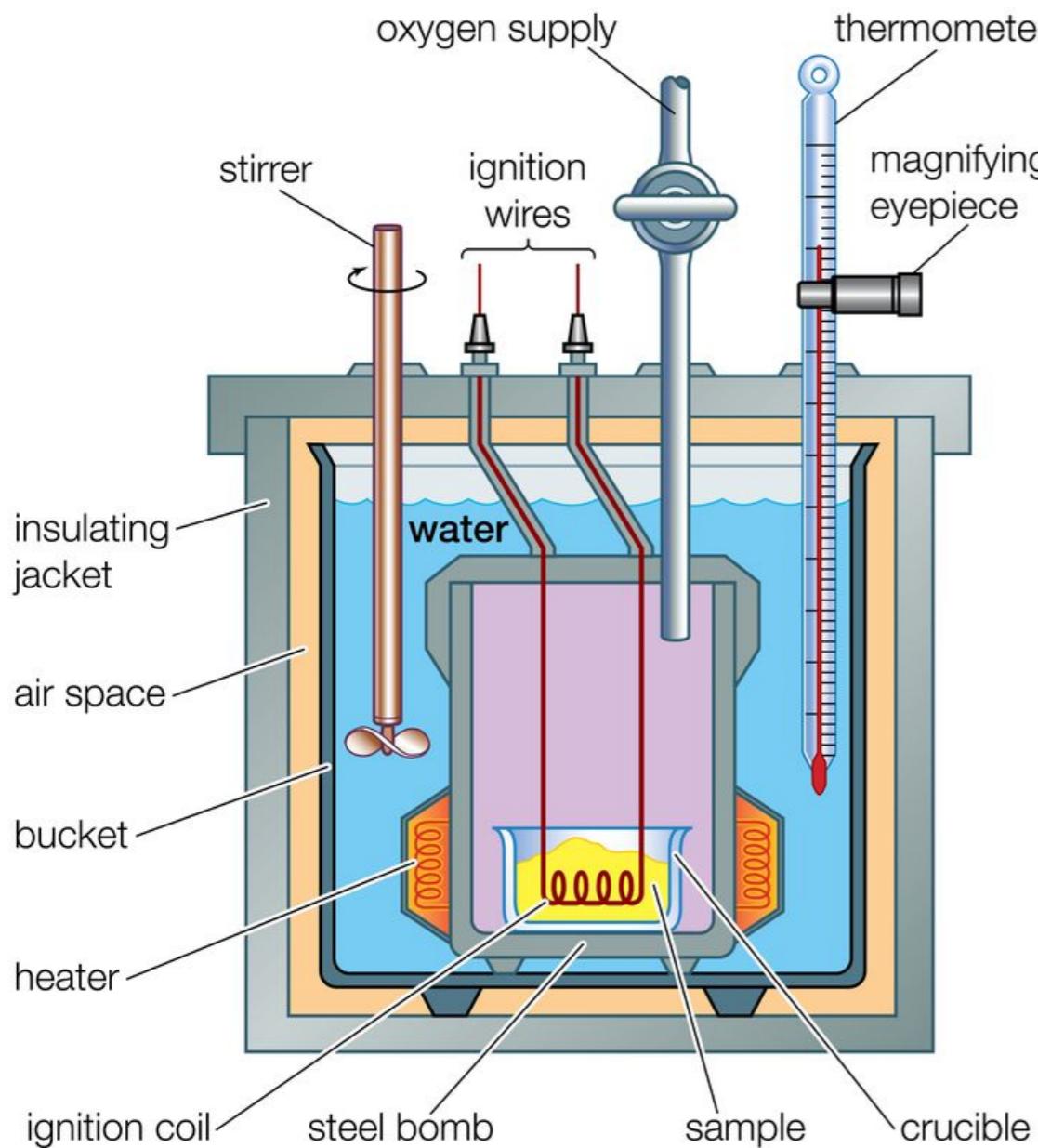


H_2 is a reference species so
 $\Delta_f H_{\text{H}_2}^\circ = 0$

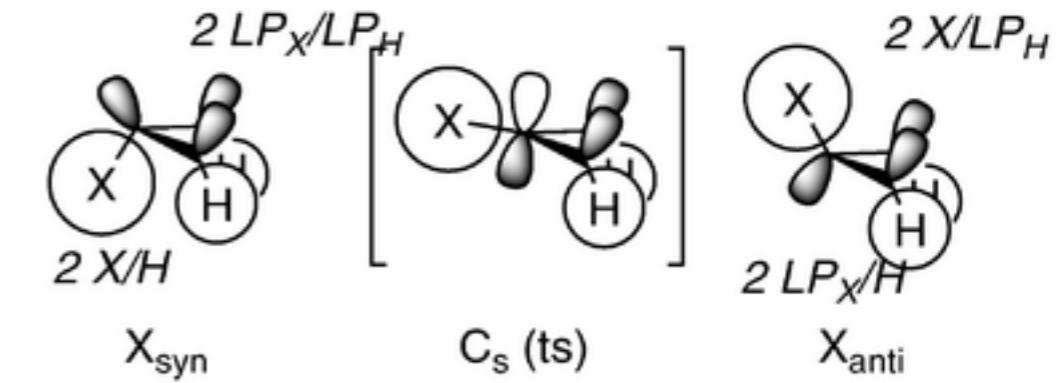


H_2O is not a reference species so
 $\Delta_f H_{\text{H}_2\text{O}}^\circ \neq 0$

Measuring / Computing Enthalpy of Formation



Bomb Calorimeter



Quantum Chemistry

Bond Energy Method

Bond	Avg. Energy (kJ/mol)	Avg. Length (Å)
H–H	432	0.74
N–N	167	1.45
F–F	155	1.42
O–O	142	1.48
H–F	565	0.92
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Step 1 - Write down the formation reaction

Step 2 - Assume all bonds are “average” bonds

Step 3 - Count bonds and add them up!

$$\begin{aligned}\Delta_f H_{H_2O}^\circ &= 2 \times (\text{H–O}) - [1 \times (\text{H–H}) + \frac{1}{2} \times (\text{O=O})] \\ &= (2)(459) - (1)(432) - (0.5)494 \\ &= \boxed{-239 \text{ kJ/mol}}\end{aligned}$$

Actual value \rightarrow -242 kJ/mol

Beware! Breaks down for highly polar or strained molecules

Tabulated and Polynomial Data

Compiled sets of reference properties such as [JANAF Tables](#)

Water (H ₂ O)				$\Delta h^\circ(T)$	H ₂ O ₁ (g)		
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
				$\text{J}\cdot\text{K}^{-1}\text{ mol}^{-1}$			
0	0.	0.	INFINITE	-9.904	-238.921	-238.921	INFINITE
100	33.299	152.388	218.534	-6.615	-240.083	-236.584	123.579
200	33.349	175.485	191.896	-3.282	-240.900	-232.766	60.792
298.15	33.590	188.834	188.834	0.	-241.826	-228.582	40.047
300	33.596	189.042	188.835	0.062	-241.844	-228.500	39.785

Often polynomial fits used for speed/utility in programming

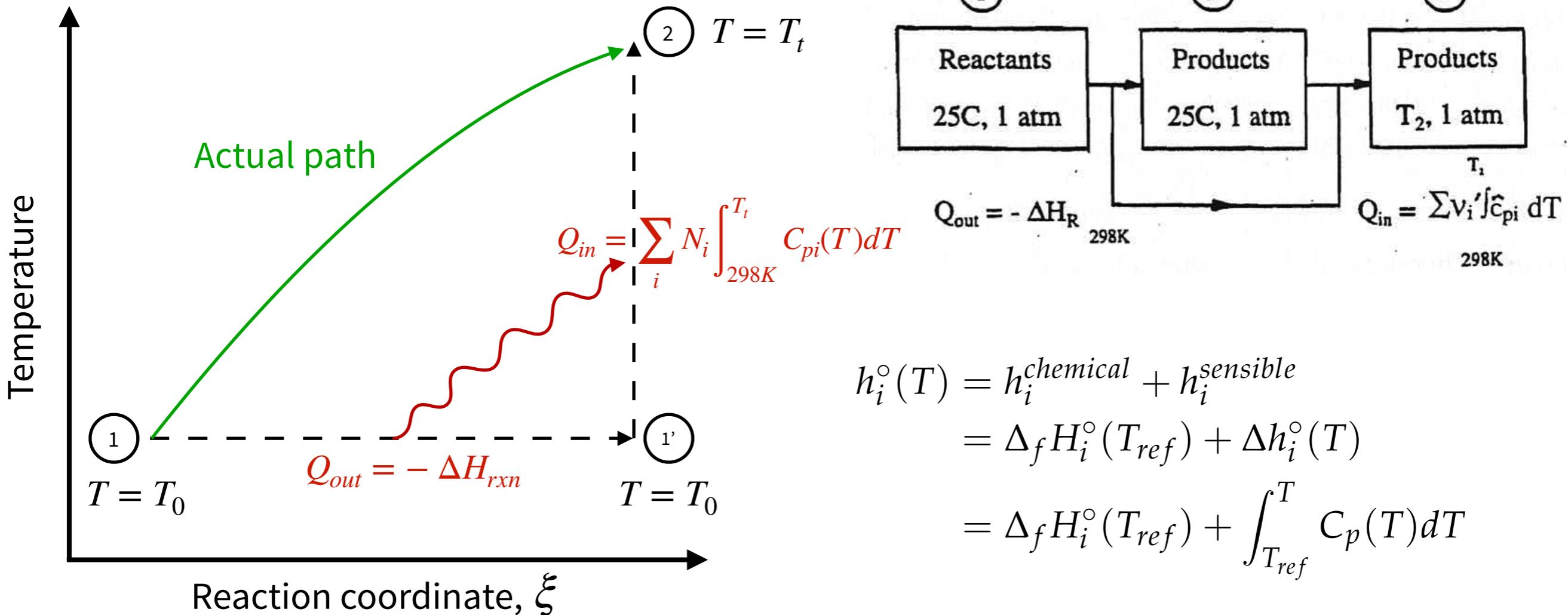
$$\frac{C_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{H}{RT} = a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 \ln T + a_2 T + a_3 \frac{T^2}{2} + a_4 \frac{T^3}{3} + a_5 \frac{T^4}{4} + a_7$$

[NASA thermodynamic polynomials](#)

Adiabatic Combustion



$$\begin{aligned}
 h_i^\circ(T) &= h_i^{chemical} + h_i^{sensible} \\
 &= \Delta_f H_i^\circ(T_{ref}) + \Delta h_i^\circ(T) \\
 &= \Delta_f H_i^\circ(T_{ref}) + \int_{T_{ref}}^T C_p(T) dT
 \end{aligned}$$

$$\Delta H_{rxn}^\circ = \sum_I n_i \Delta_f H_i^\circ(T_{ref})|_{product} - \sum_I n_i \Delta_f H_i^\circ(T_{ref})|_{reactant}$$

If reactants at T_{ref} :

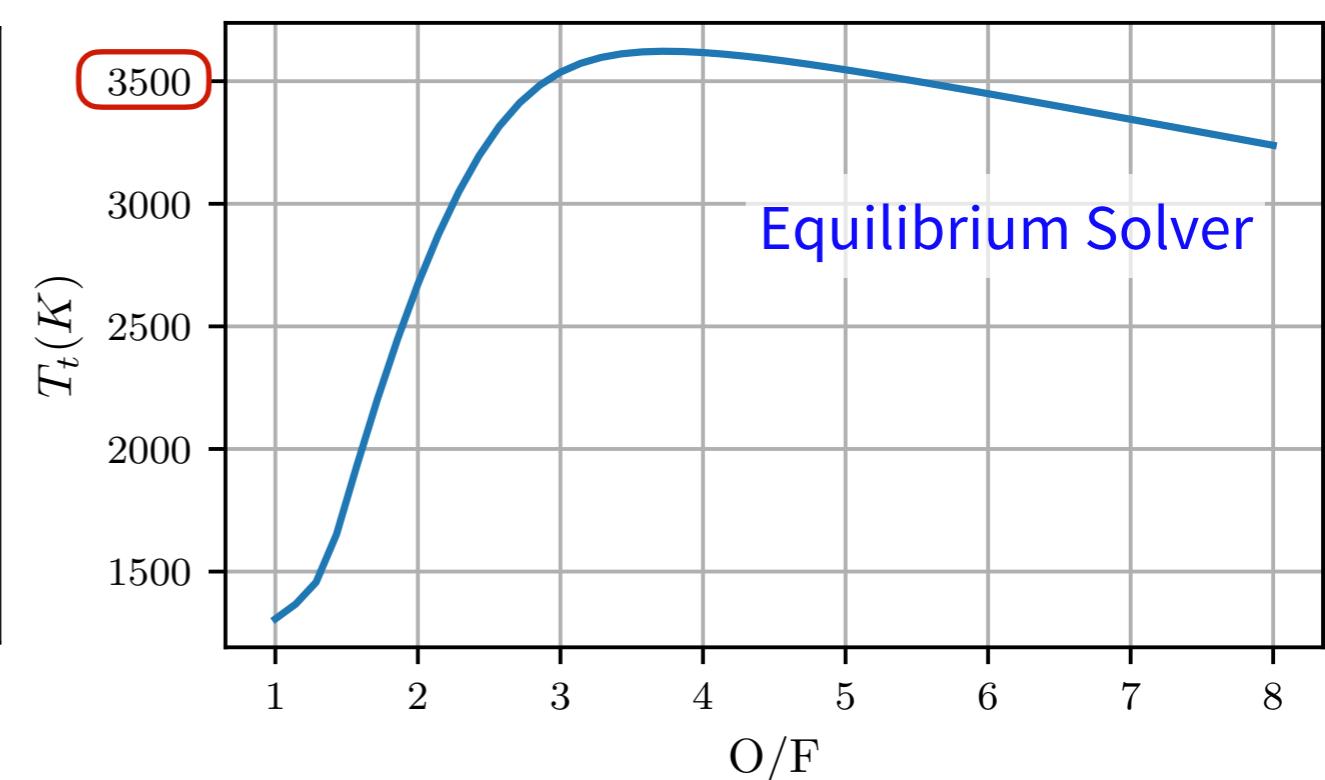
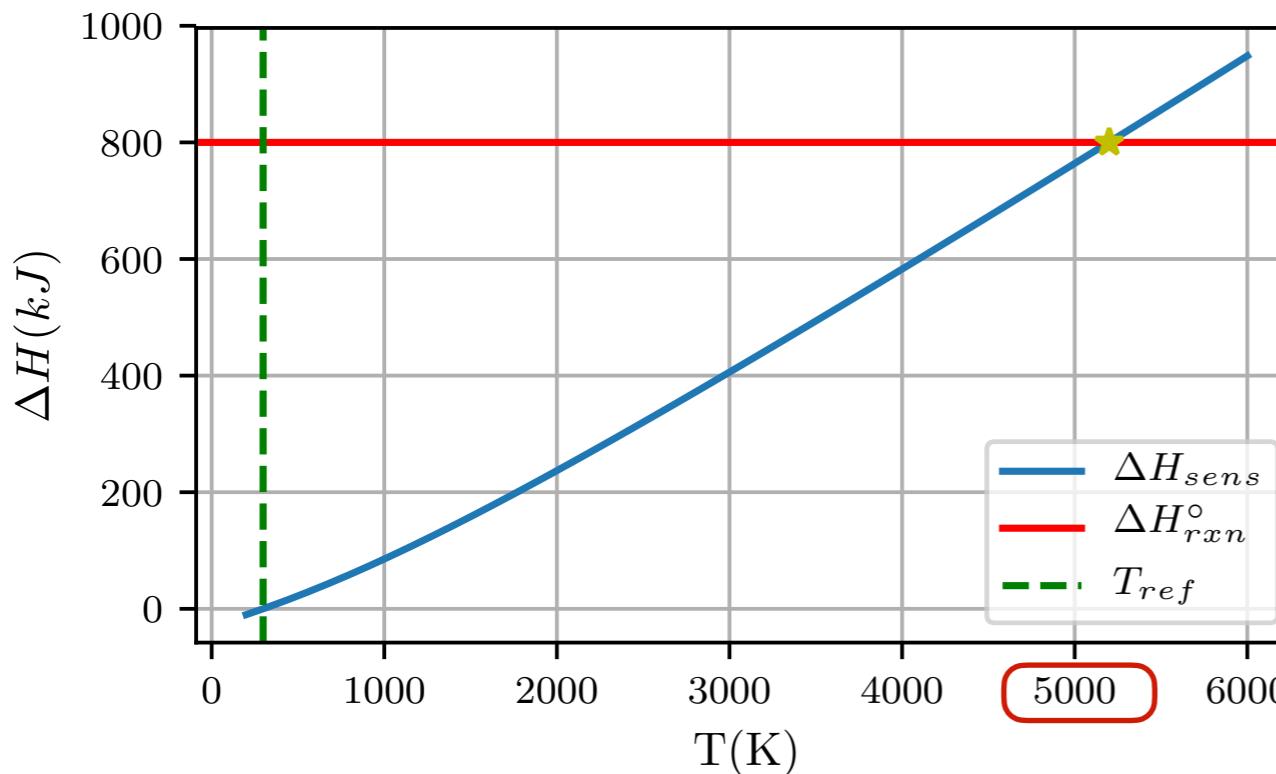
$$-\Delta H_{rxn}^\circ = \sum_I n_i \Delta h_i^\circ(T)|_{product} = \sum_I n_i \int_{T_{ref}}^T C_p(T) dT|_{product}$$

A first try

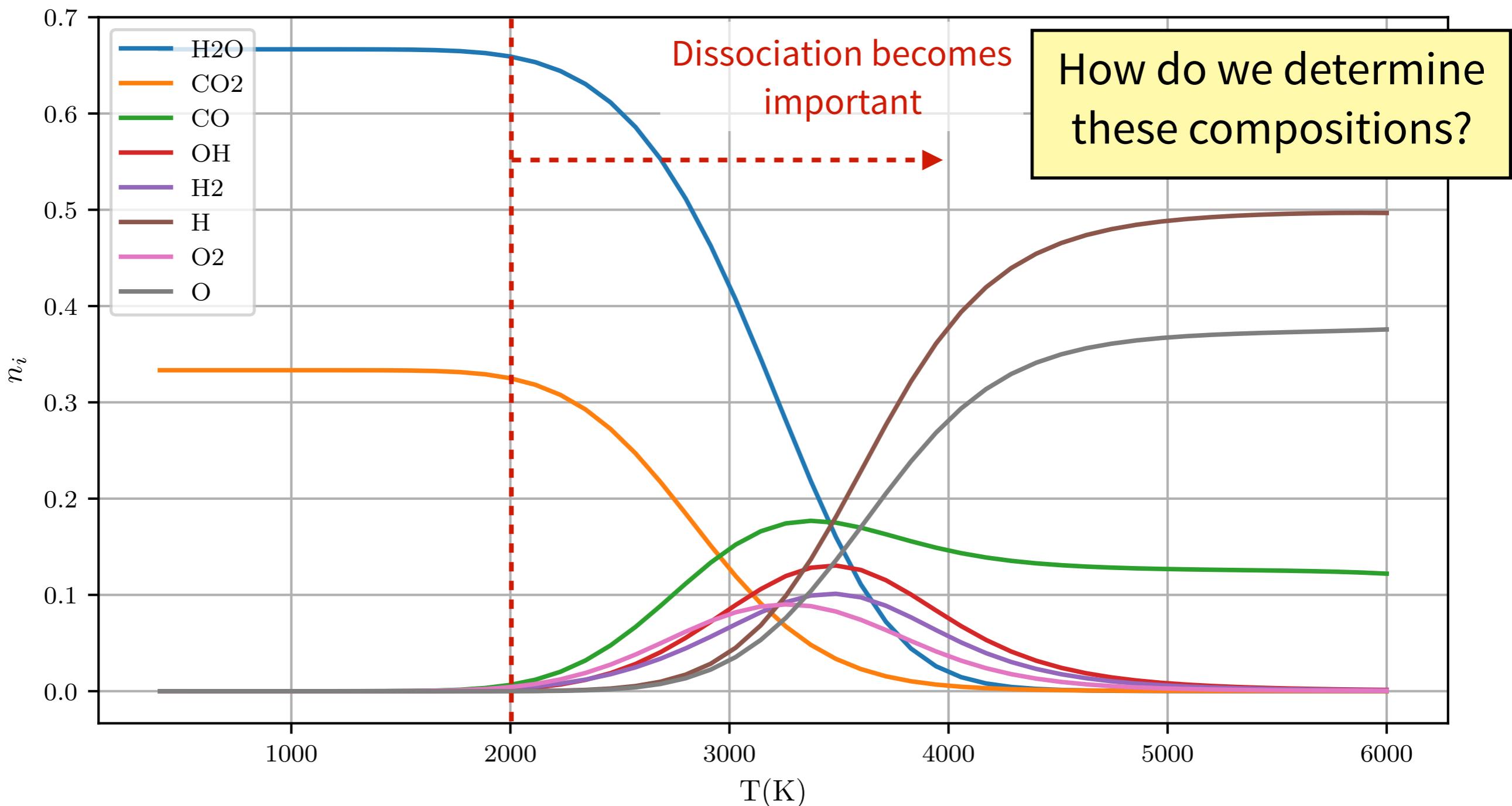


$$\begin{aligned}
 \Delta H_{rxn}^\circ &= \sum^N n_i \Delta_f H_i^\circ(T_{ref})|_{product} - \sum^N n_i \Delta_f H_i^\circ(T_{ref})|_{reactant} \\
 &= 2 \times \Delta_f H_{\text{H}_2\text{O}}^\circ + \Delta_f H_{\text{CO}_2}^\circ - 2 \times \Delta_f H_{\text{O}_2}^\circ - \Delta_f H_{\text{CH}_4}^\circ \\
 &= (2)(-240) + (-394) - (-75) \\
 &= 800 \text{ kJ}
 \end{aligned}$$

Our first try is way off!
Why??

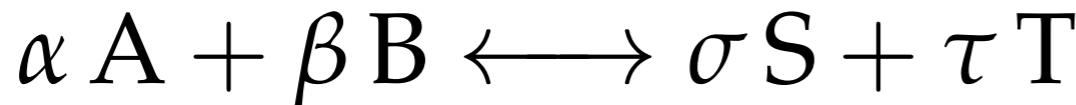


Complex Equilibria



Law of Mass Action

First there was the Law of Mass Action



$$r_f = k_+ [A]^\alpha [B]^\beta$$

$$k_+ [A]^\alpha [B]^\beta = k_- [S]^\sigma [T]^\tau$$

Key insight was that at equilibrium reaction rates of forward and backward reaction are equal

$$K_c = \frac{k_+}{k_-} = \frac{[S]^\sigma [T]^\tau}{[A]^\alpha [B]^\beta}$$

This is the modern equilibrium constant equation!

Ueber die chemische Affinität;

von

C. M. Guldberg und P. Waage.

§ 1. Einleitung.

Im Jahre 1867 haben wir unter dem Titel: „Etudes sur les affinités chimiques“ eine Arbeit über die chemische Affinität veröffentlicht¹⁾), in welcher wir uns vorzüglich mit der chemischen Massenwirkung beschäftigten. Wir sprachen es als unsere Anschauung aus, dass das Resultat eines chemischen Prozesses nicht allein von denjenigen Stoffen abhängt, welche in die neue chemische Verbindung eingehen, sondern auch von allen anderen bei dem Prozesse gegenwärtigen Stoffen, welche letztere wir mit einem gemeinschaftlichen Namen als fremde Stoffe bezeichneten, insofern dieselben einen merkbaren Einfluss ausüben, obwohl sie selbst keine chemische Veränderung während des Prozesses erleiden. Zu diesen fremden Stoffen rechneten wir namentlich auch die Auflösungsmittel.

Die chemischen Kräfte, welche zwischen den Stoffen in

¹⁾ Vergl. Topsøe's vorzügliche Zusammenstellung in Tidsskrift for Physik og Chemi. Bd. 8, 12.

²⁾ Als Universitätsprogramm erschienen. 1. Semester 1867.

Guldberg & Waage, 1879

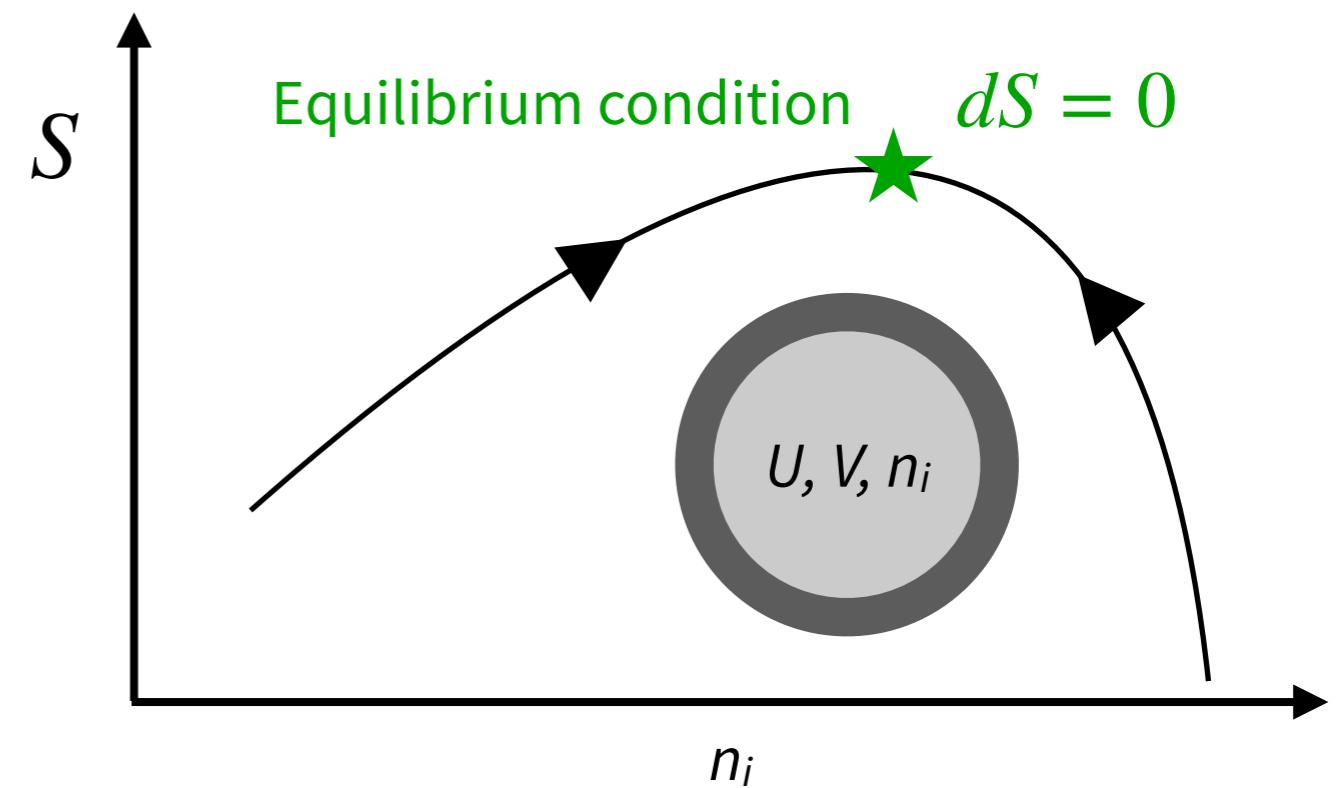
$$K_p = K_c (RT)^{\sum I N_{ip} - N_{ir}}$$

Equilibrium States

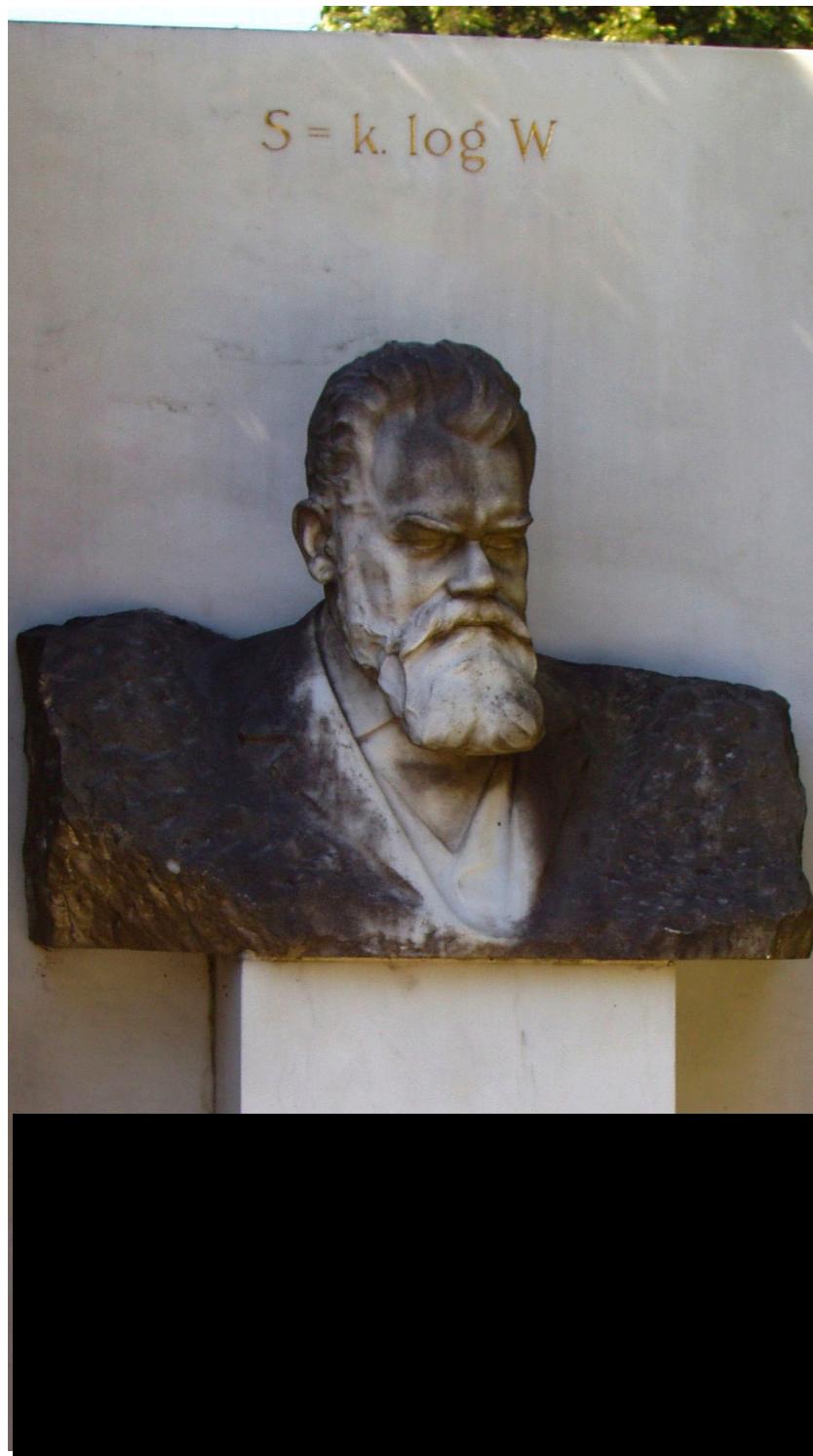
Thermodynamic equilibrium is the state of the system where flows and potentials are balanced. The second law states for an isolated system $dS \geq 0$. Equilibrium is achieved when the equality holds such that entropy is at a maximum.

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,n_i} dU + \left(\frac{\partial S}{\partial V}\right)_{U,n_i} dV + \sum_{i=1}^I \left(\frac{\partial S}{\partial n_i}\right)_{U,V,N_j \neq n_i} dn_i$$

degrees of freedom
 $F = C - P + 2 = 1 + C$
(Gibbs phase rule)

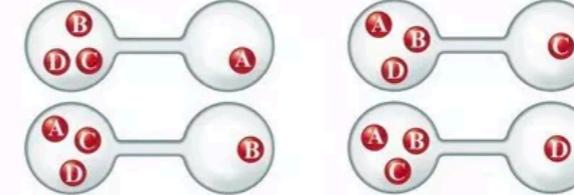
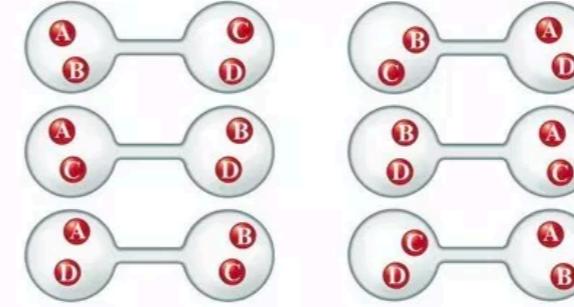
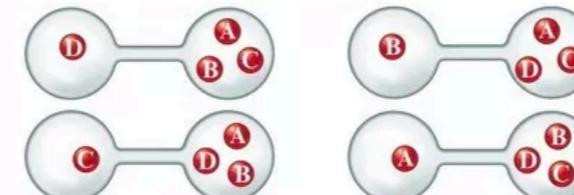


What is Entropy?



$$S = k_B \ln \Omega$$

Table 17.1 | The Microstates That Give a Particular Arrangement (State)

Arrangement	Microstates	Number of Microstates
I		1
II		4
III		6
IV		4
V		1

Classical and Modern Entropy

V_1, T	vacuum
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$2V_1, T$

What is the change in entropy?

StatsMech

$$S = k_B \ln \Omega \quad \Omega \propto V \Rightarrow \frac{\Omega_f}{\Omega_0} = \frac{V_f}{V_0} = 2$$

$$S_2 - S_1 = k_B \ln(2\Omega_1) - k_B \ln(\Omega_1) = k_B \ln(2)$$

Classical

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

$$dS = R \frac{1}{V} dV$$

$$\int_{S_0}^{S_f} = R \int_{V_0}^{V_f} \frac{1}{V} dV = S_f - S_0 = R \ln \left(\frac{V_f}{V_0} \right) = R \ln(2)$$

$$k_B = \frac{R}{N_A}$$

Multi-component Equilibrium

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,n_i} dU + \left(\frac{\partial S}{\partial V} \right)_{U,n_i} dV + \sum_{i=1}^I \left(\frac{\partial S}{\partial n_i} \right)_{U,V,N_j \neq n_i} dn_i$$

$$\left(\frac{\partial S}{\partial U} \right)_{V,n_i} \equiv \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V} \right)_{U,n_i} \equiv \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial n_i} \right)_{P,T,N_j \neq n_i} \equiv -\frac{\mu_i}{T}$$

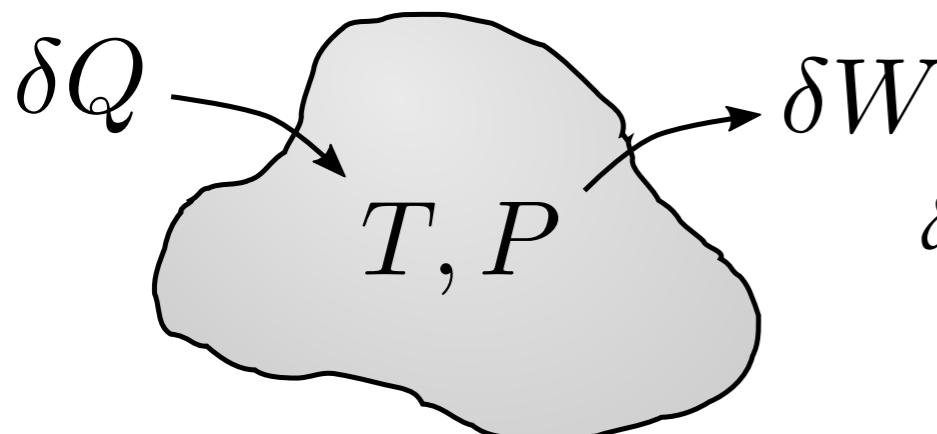
$$dS_{U,V} = - \sum_{i=1}^I \frac{\mu_i}{T} dn_i.$$

μ_i is called the *chemical potential*

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_{i=1}^I \frac{\mu_i}{T} dn_i$$

The complete Gibbs Equation

Constant T, P multi-component equilibrium



First Law

$$\delta W - \delta Q + dU = (PdV - \cancel{VdP})^0 - \delta Q + dU = 0$$

$$dS - \frac{\delta Q}{T} \geq 0$$

Second Law

$$TdS - dU - PdV \geq 0$$

$$TdS - dU - PdV = d[TS - (U + PV)]_{P,T} = d[TS - H]_{P,T}$$

$$G \equiv H - TS$$

\Rightarrow

$$dG_{T,P} \leq 0.$$

$$G = G(P, T, N_1, \dots N_I)$$

Constant T,P Multi-component Equilibrium

$$dG \equiv \left(\frac{\partial G}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T,n_i} dP + \sum_I \left(\frac{\partial G}{\partial n_i} \right)_{P,T,N_j \neq n_i} dn_i$$

$$\begin{aligned} \left(\frac{\partial G}{\partial T} \right)_{P,n_i} dT &\equiv -S \\ \left(\frac{\partial G}{\partial P} \right)_{T,n_i} dP &\equiv V \end{aligned} \quad \left(\frac{\partial G}{\partial n_i} \right)_{P,T,N_j \neq n_i} = \mu_i. \quad \Rightarrow \quad \boxed{\mu_i = g_i}$$

Chemical potential is equivalent to the *partial molal gibbs energy*, a very useful result!! At equilibrium:

$$dG = 0 = \sum_{Products} n_i \mu_i - \sum_{Reactants} n_i \mu_i = \sum_I (N_{i_p} - N_{i_r}) g_i$$

Partial Gibbs Energy

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \quad \text{Gibbs Equation}$$

For fixed, T : $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$ (From ideal gas law)

$$ds_i = -R \frac{dP_i}{P_i}$$

$$dg_i = -Tds_i(T, P_i) \quad dg_i = -TdS_i(T, P_i) = RT \frac{dP_i}{P_i}$$

Integrate $\Rightarrow g_i(T, P_i) - g_i(T, P^\circ) = RT \ln \left(\frac{P_i}{P^\circ} \right)$

$$\Rightarrow \sum_I (N_{i_p} - N_{i_r})g_i(T, P^\circ) + RT \sum_I (N_{i_p} - N_{i_r}) \ln \left(\frac{P_i}{P^\circ} \right) = 0.$$

where $g_i(T, P^\circ) = g_i^\circ(T)$

standard molal Gibbs energy is only a function of temperature!

Equilibrium Constant

$$\Delta G^\circ(T) = \sum_I (N_{i_p} - N_{i_r}) g_i^\circ(T) \quad \prod_I \left[\frac{P_i}{P^\circ} \right]^{N_{i_p} - N_{i_r}} = e^{\left(\frac{-\Delta G^\circ(T)}{RT} \right)}$$

Defining a Gibbs heat of formation similarly to Enthalpy of Formation

$$\Rightarrow K_p(T) = \prod_I \left[\frac{P_i}{P^\circ} \right]^{N_{i_p} - N_{i_r}} = e^{\left(\frac{-\sum_I (N_{i_p} - N_{i_r}) \Delta_f G_i^\circ(T)}{RT} \right)}$$

If P_i are partial pressures so that $P_i = X_i P$ and we recognize $\log P^\circ = 0$

$$\log K_p(T) = \sum_{prod} N_i \log X_i - \sum_{react} N_i \log X_i + (N_P - N_R) \log P$$

Le Chatelier's Principle

Equilibrium Constants

$$\log K_p(T) = \sum_{prod} \log K_{pfi} - \sum_{react} \log K_{pfi}$$

Formation equilibrium constants

$$K_p(T) = \prod_I \left[\frac{P_i}{P^\circ} \right]^{N_{ip} - N_{ir}} = e^{\left(\frac{-\sum_I (N_{ip} - N_{ir}) \Delta_f G_i^\circ(T)}{RT} \right)}$$

Water (H₂O)

H₂O₁(g)

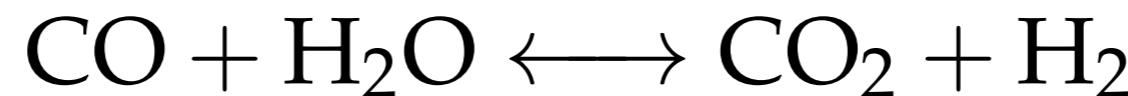
Enthalpy Reference Temperature = T_r = 298.15 K

Standard State Pressure = p° = 0.1 MPa

Remember JANAF Tables?

T/K	J·K ⁻¹ mol ⁻¹				kJ·mol ⁻¹	Δ _f H°	Δ _f G°	log K _f
	C _p °	S°	-[G° - H°(T _r)]/T	H-H°(T _r)				
0	0.	0.	INFINITE	-9.904	-238.921	-238.921	INFINITE	
100	33.299	152.388	218.534	-6.615	-240.083	-236.584	123.579	
200	33.349	175.485	191.896	-3.282	-240.900	-232.766	60.792	
298.15	33.590	188.834	188.834	0.	-241.826	-228.582	40.047	

Water gas shift (WGS) reaction



$$\log_{10} \left(\frac{X_{\text{CO}_2} X_{\text{H}_2}}{X_{\text{H}_2\text{O}} X_{\text{CO}}} \right) = \log_{10} K_{pf_{\text{CO}_2}}(T) + \log_{10} K_{pf_{\text{H}_2}}(T) - \\ \log_{10} K_{pf_{\text{H}_2\text{O}}}(T) - \log_{10} K_{pf_{\text{CO}}}(T)$$

Equilibrium
Constant

$$2X_{\text{CO}_2} + X_{\text{H}_2\text{O}} + X_{\text{CO}} = 2$$

Oxygen balance

$$X_{\text{CO}_2} + X_{\text{CO}} = 1$$

Carbon balance

$$X_{\text{H}_2} + X_{\text{H}_2\text{O}} = 2$$

Hydrogen balance

4 Equations

If we chose a T , there are also 4 unknowns $X_{\text{CO}_2}, X_{\text{H}_2}, X_{\text{H}_2\text{O}}, X_{\text{CO}}$

In general, for equilibrium of **M species** consisting of **N atoms**, we must write **M - N reactions** and associate equilibrium equations to solve

Water gas shift reaction

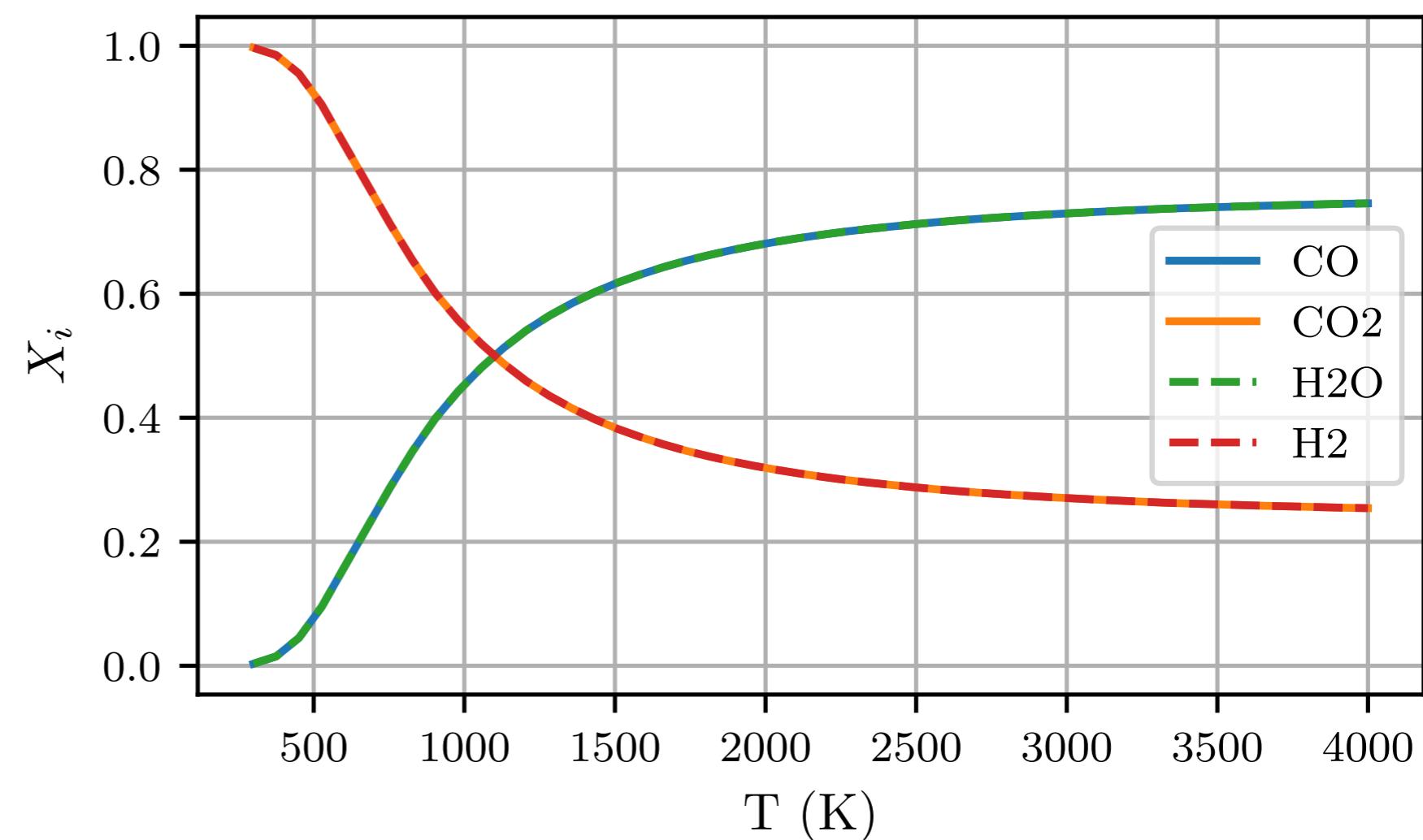
WGS is solvable in closed form

$$X_{CO} = \frac{1}{\sqrt{K_p} + 1}$$

$$X_{CO_2} = 1 - X_{CO}$$

$$X_{H_2O} = X_{CO}$$

$$X_{H_2} = 1 - X_{CO}$$



More complex equilibria get very messy this way!

Element Potentials

Goal: Reduced book-keeping for equilibrium calculations

$$\sum_I \eta_{ij} n_i = a_j$$

$$d \left[G + \sum_J \lambda_j \left(\sum_i \eta_{ij} n_i - a_j \right) \right]_{T,P} = 0$$

Method of Lagrange Multipliers

$$dG_{T,P} - \sum_J \lambda_j \sum_I \eta_{ij} dn_i = \sum_I \left(g_i - \sum_J \eta_{ij} \lambda_j \right) dn_i = 0. \quad g_i = \sum_J \eta_{ij} \lambda_j$$

$$g_i = h_i - T s_i(X_i) \rightarrow \frac{\partial g_i}{\partial X_i} = T \frac{\partial s_i}{\partial X_i} \quad \frac{\partial s_i}{\partial X_i} = R \ln X_i$$

$$\frac{g_i}{RT} + \ln X_i + \frac{1}{RT} \sum_J \eta_{ij} \lambda_J = 0$$

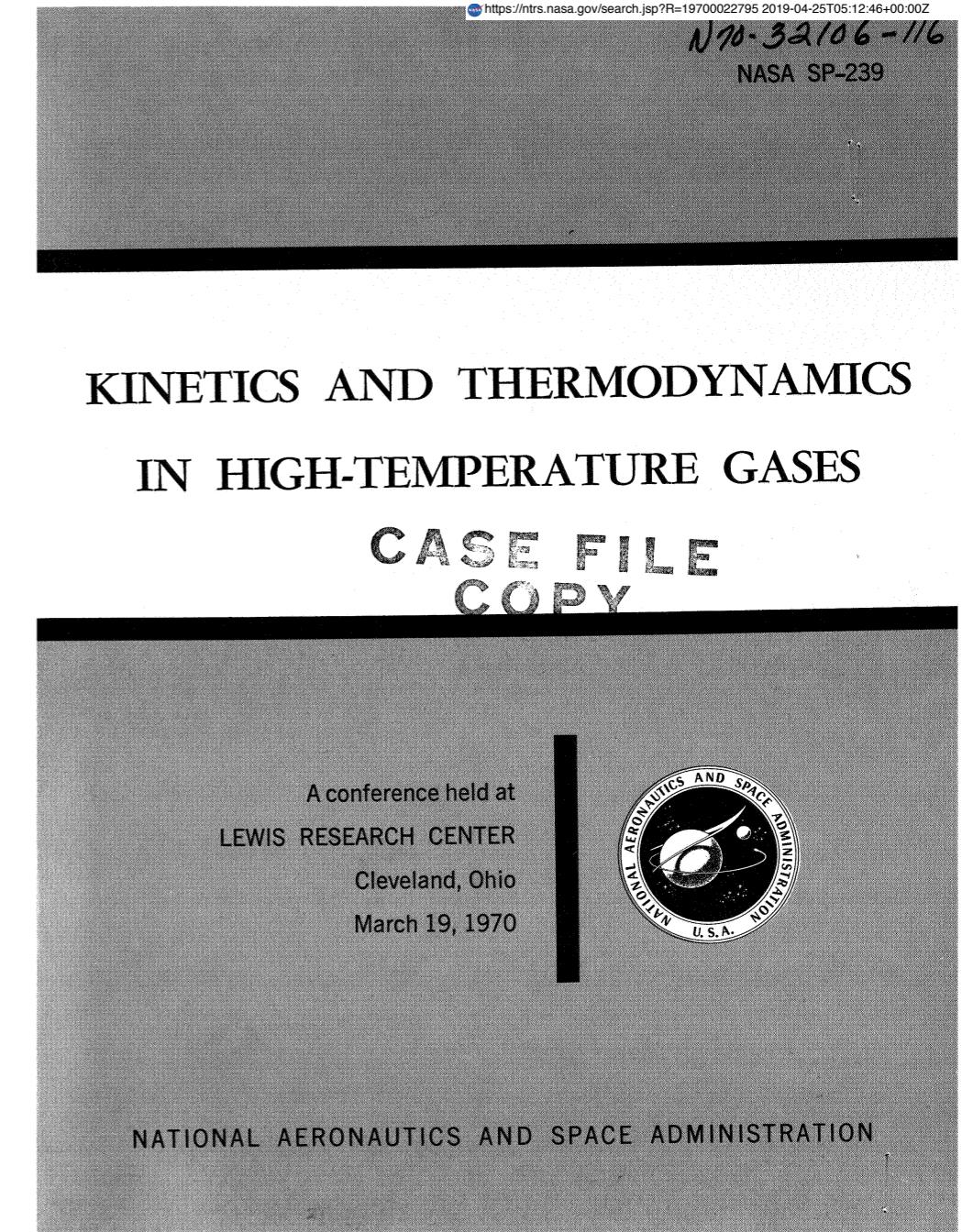
Element potentials are analogous to chemical potentials

Element Potentials

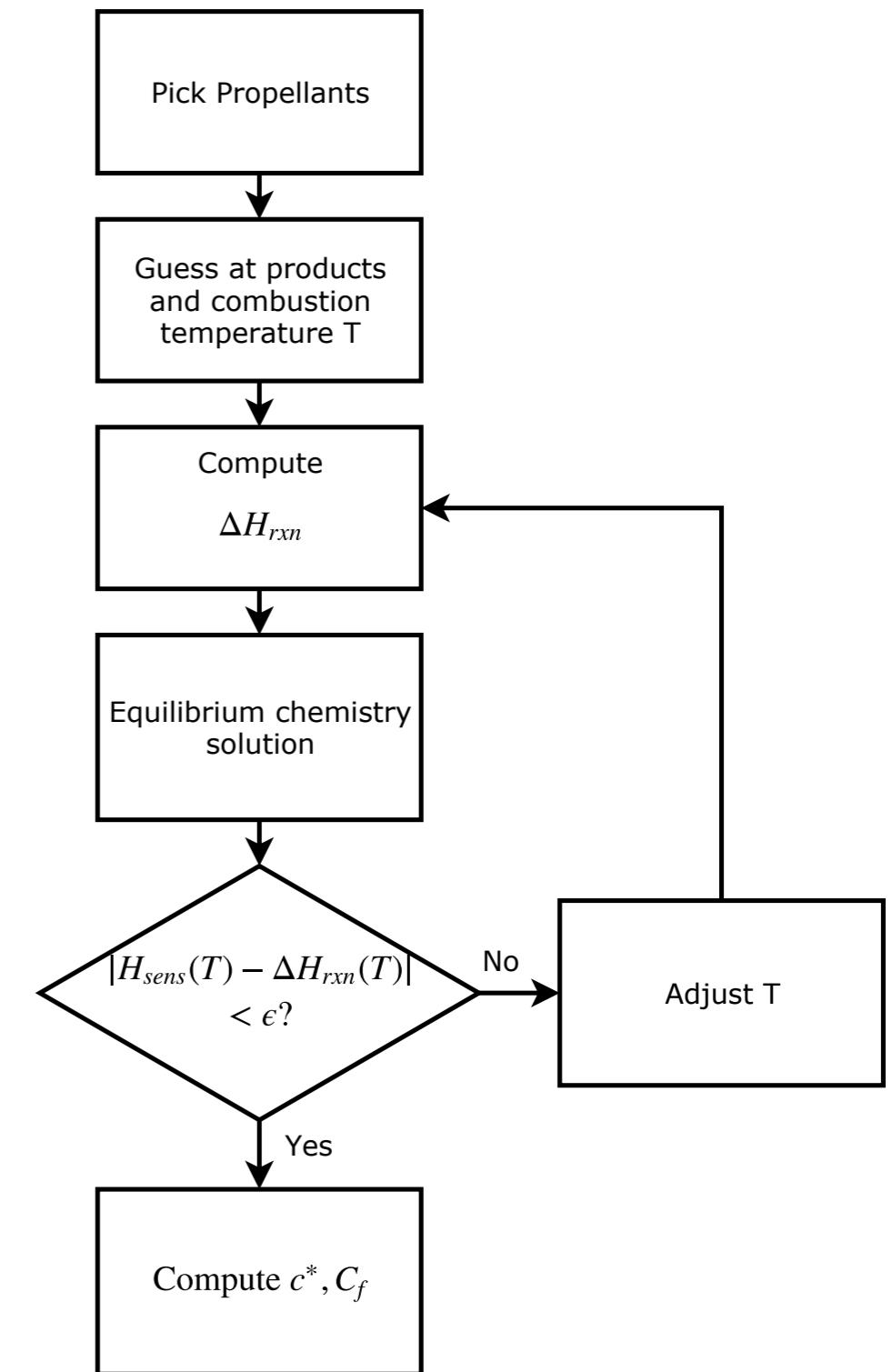
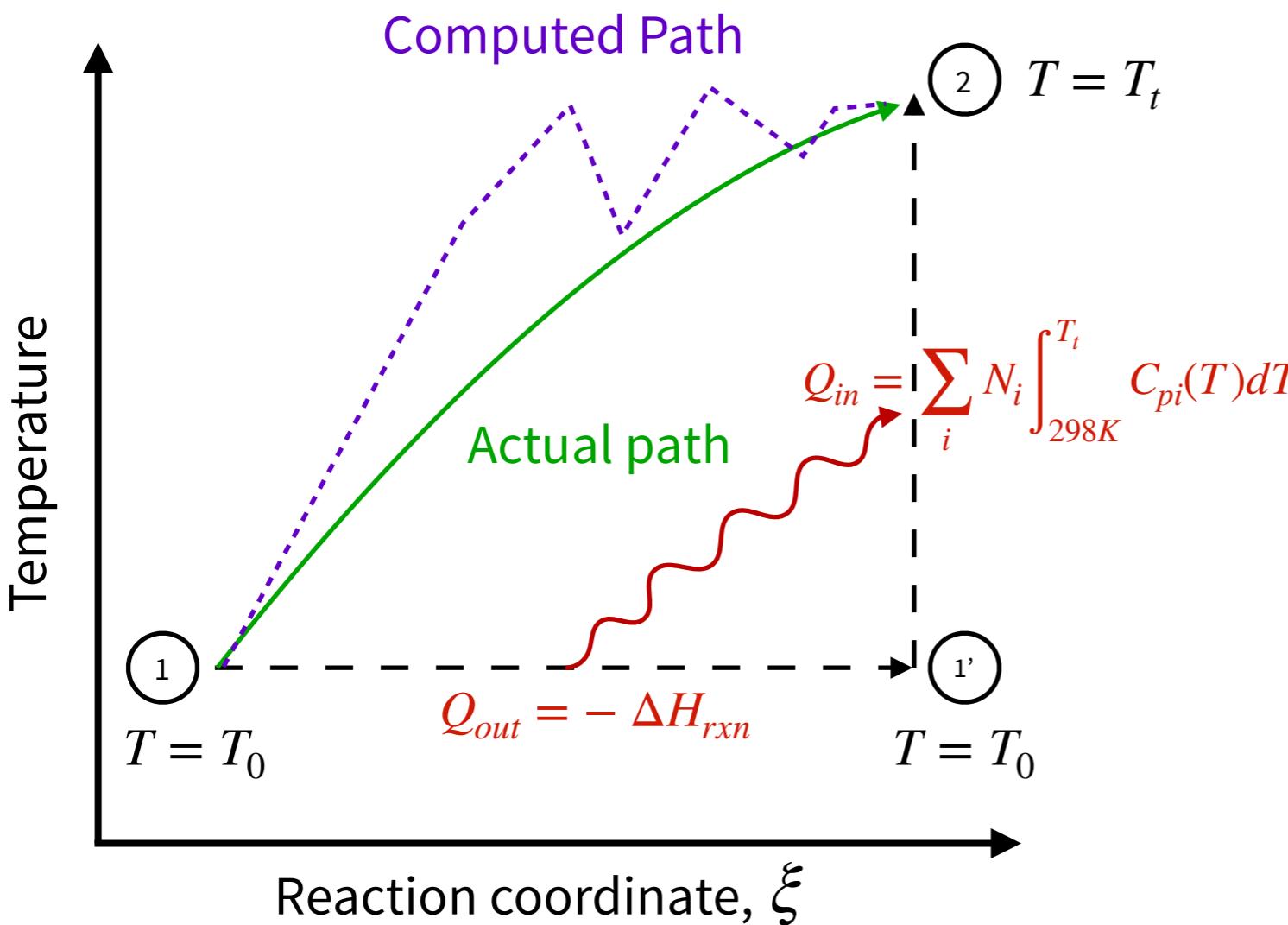
$$\frac{g_i}{RT} + \ln X_i + \frac{1}{RT} \sum_J \eta_{ij} \lambda_J = 0$$

No need to write out chemical reactions, one equations per species.

For many species there may be more equations with element potentials (due to addition of Lagrange Multipliers), but developing the equations is straightforward

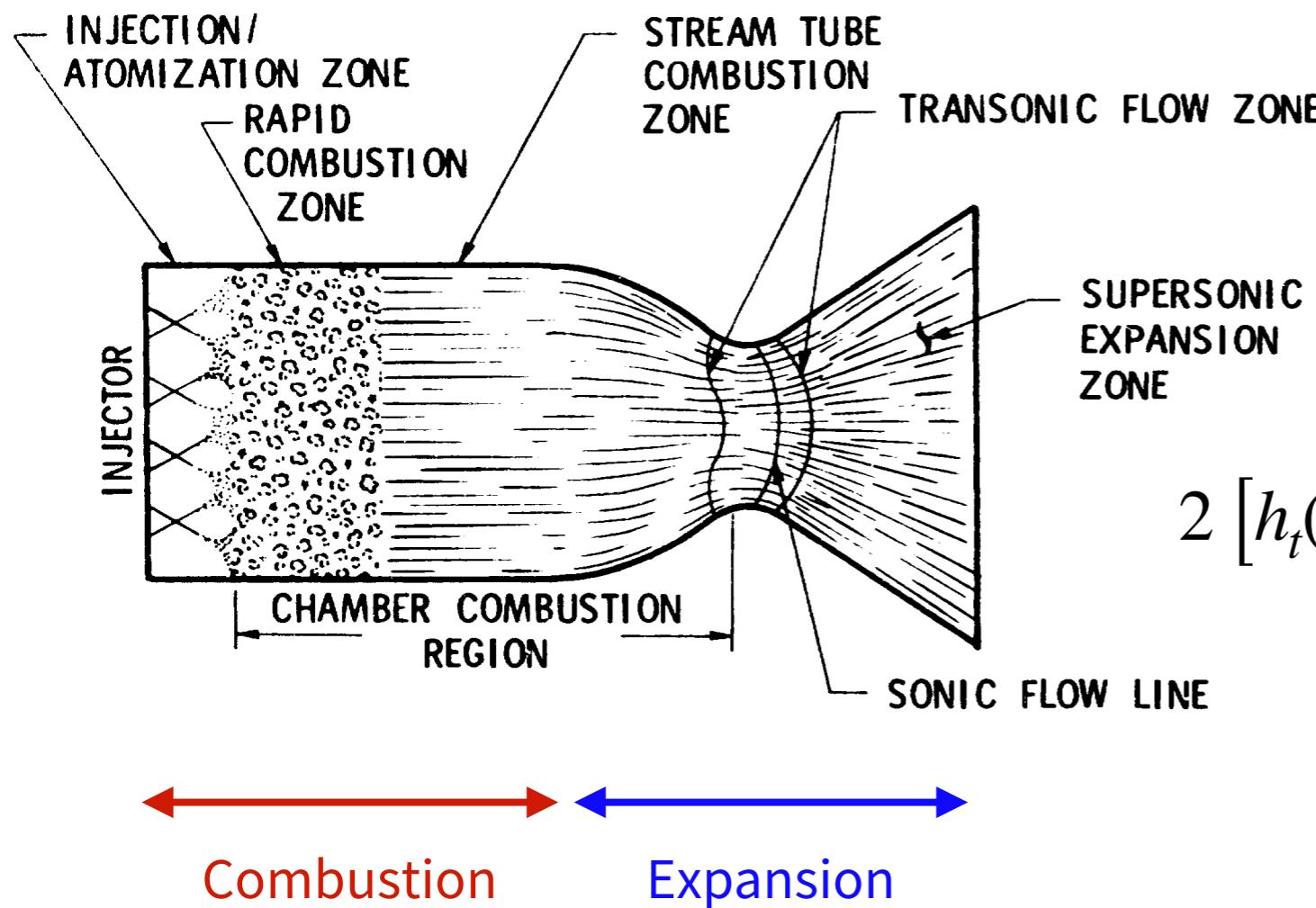


Rocket Performance Calculation



Rocket Performance Calculation

LIQUID ROCKET ENGINE STEADY STATE OPERATION



During expansion, lower P at constant s and solve for throat condition

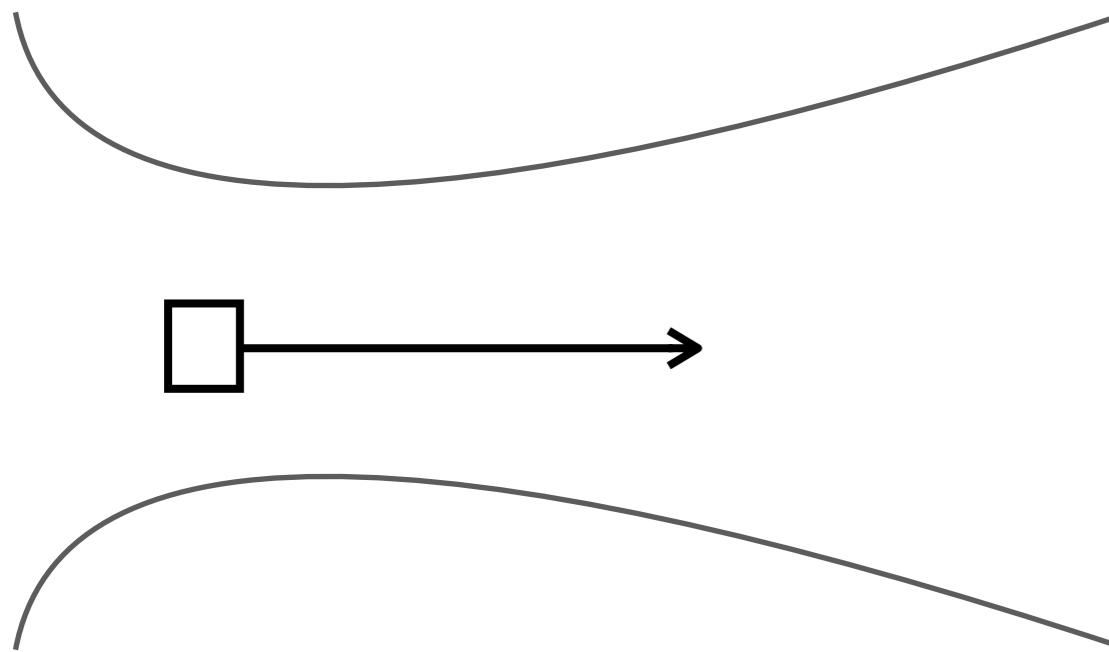
$$\Delta h = \frac{a^2}{2}$$

$$2 [h_t(T_t, X_{ti}) - h(T, X_i)]_s = \gamma(T, X_i) \frac{R_u T}{M_w(X_i)}$$

Then continue expanding to nozzle exit condition
(either $P = P_e$ or A_e/A_t)

What do we do with the composition, X_i ?

Shifting and Frozen Flow



As gas expands it accelerates and drops in temperature. The *residency time* of the gas is

$$\tau_r = \frac{L}{V}$$

where L is a length scale associated with the nozzle

Chemical kinetics depend exponentially on temperature. At some point these **kinetics are insufficient to keep gas in equilibrium**

Solving the kinetics is very difficult, so we typically look at two bounding cases:

- **frozen equilibrium** (infinitely slow kinetics) and
- **shifting equilibrium** (infinitely fast)

$$k_r \propto e^{\frac{-E_a}{RT}}$$

For frozen, we use the combustion X_i everywhere, for shifting, we re-evaluate equilibrium at every expansion step computed in the nozzle

Some Results for CH₄ + O₂

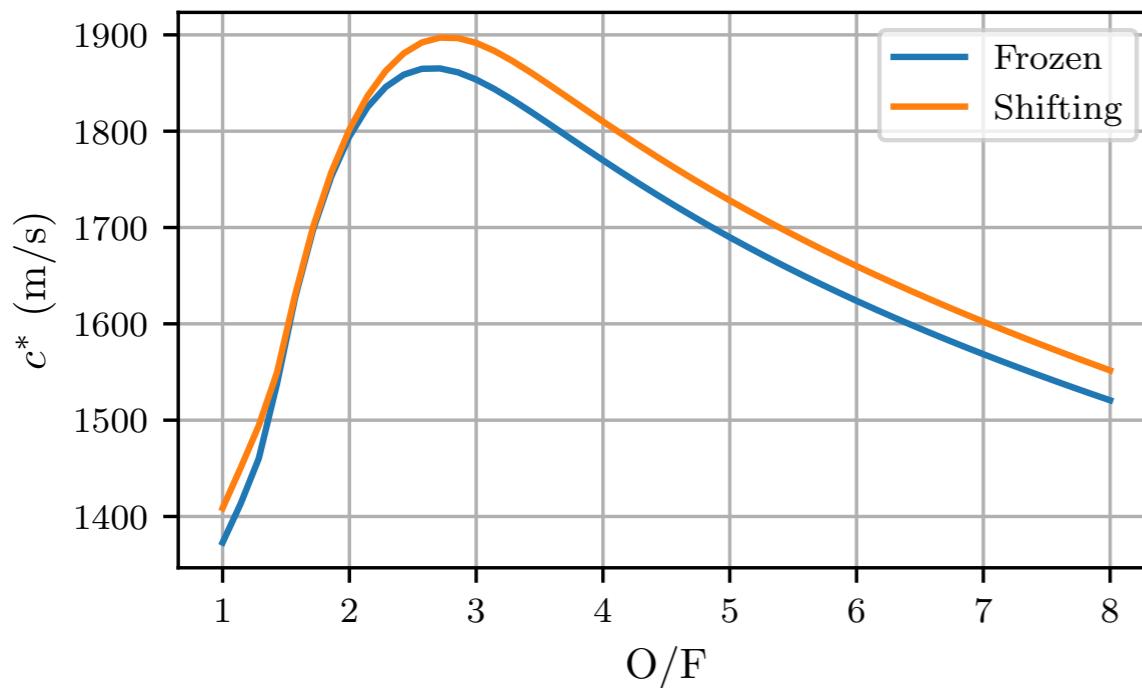


Figure 0.15: c^* as a function of O/F for the CH₄ / O₂ propellant system. Chamber pressure is set at 70 bar

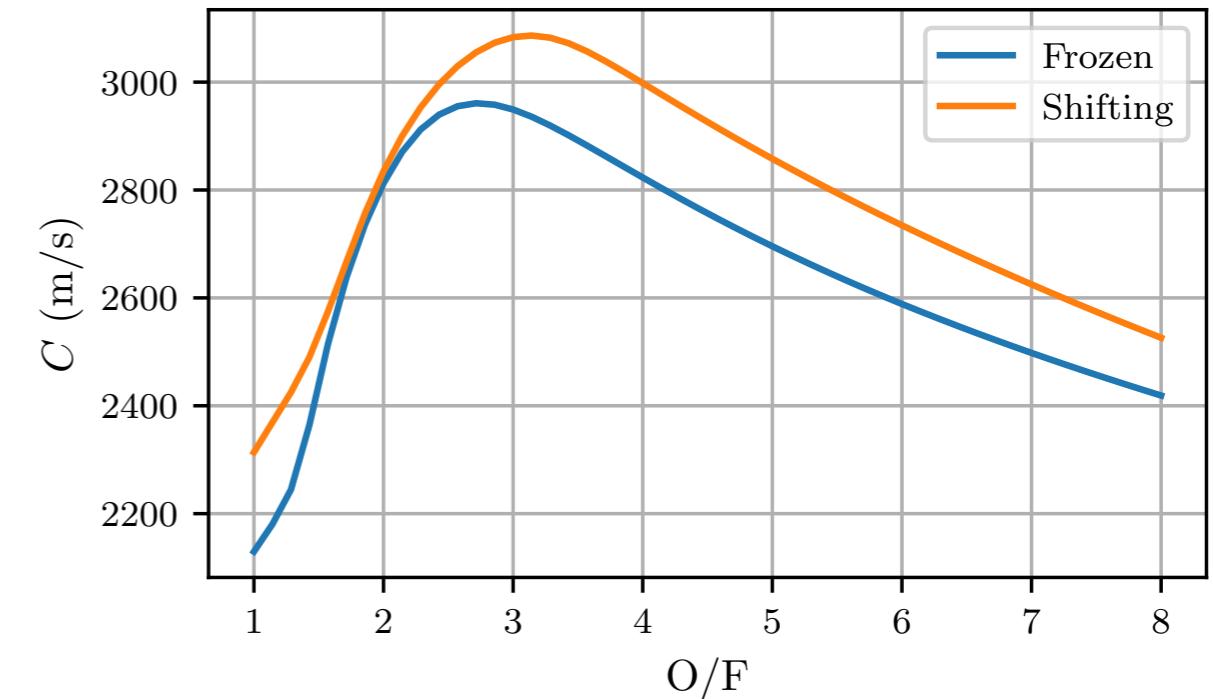
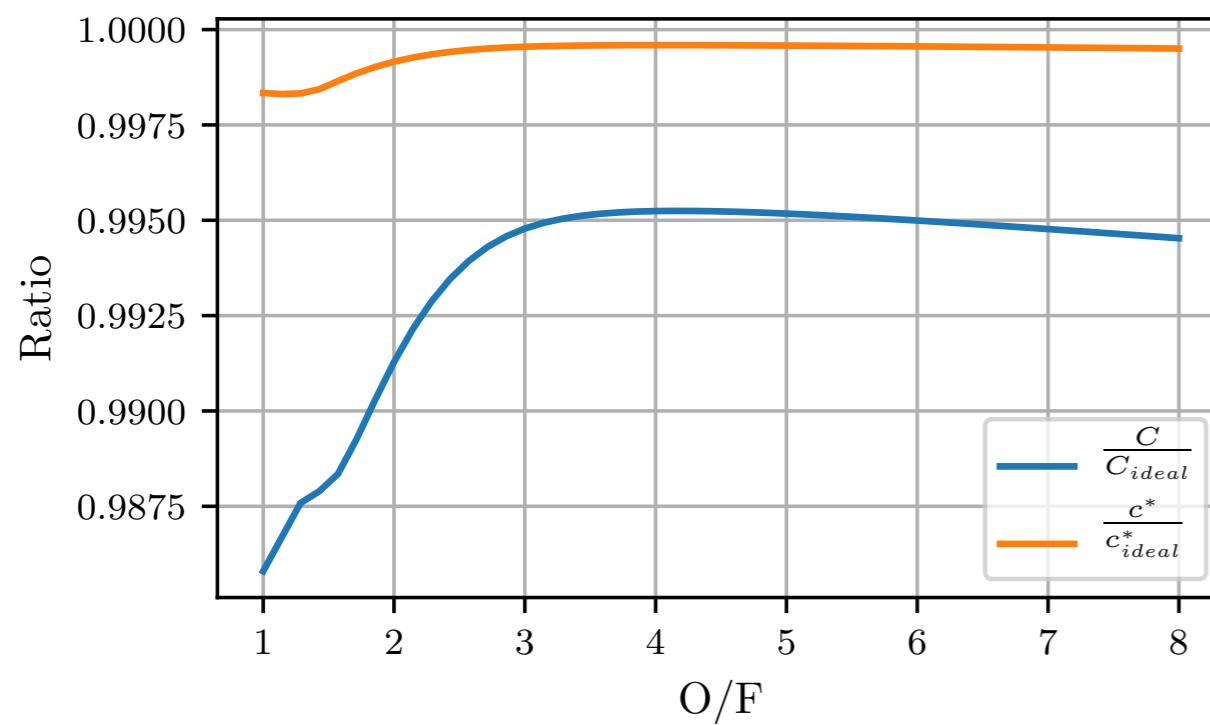
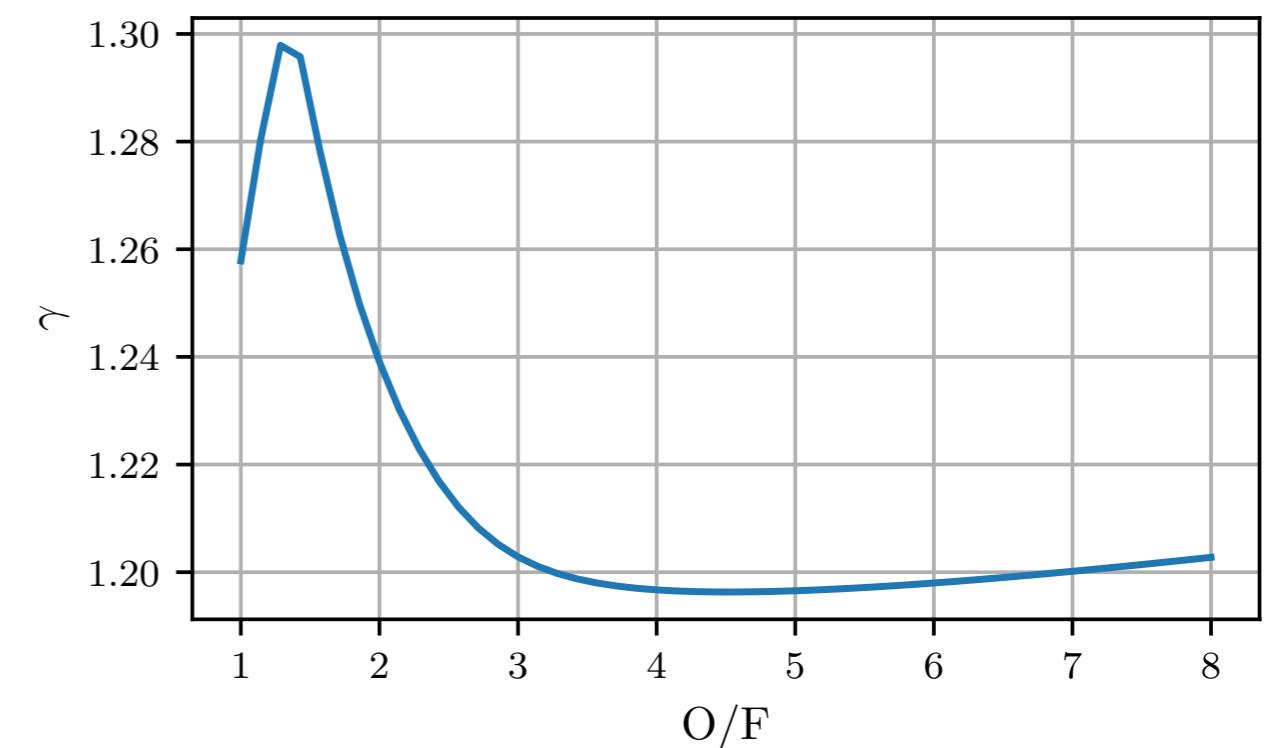
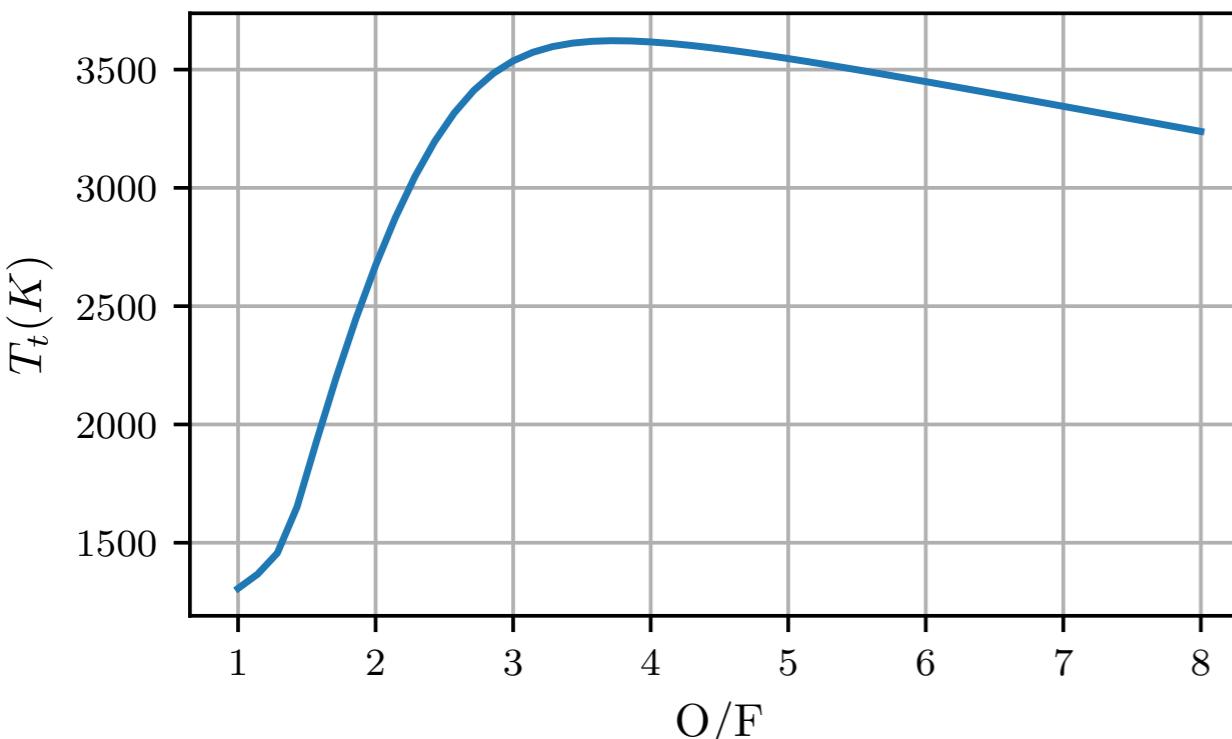


Figure 0.16: C as a function of O/F for the CH₄ / O₂ propellant system. Chamber pressure is set at 70 bar, and the exit condition is set at 1 bar pressure (so-called sea-level performance)

$$O/F = \frac{\dot{m}_{ox}}{\dot{m}_{fuel}}$$

Some Results for CH₄ + O₂



Plot to left compares detailed numerical nozzle (frozen) expansion with the analytical expressions using computed T_t , γ and molecular weight.

Other propellants

TABLE 5–5. Theoretical Performance of Liquid Rocket Propellant Combinations

Oxidizer	Fuel	Mixture Ratio		Average Specific Gravity	Chamber Temp. (K)	Chamber c^* (m/sec)	\bar{M} (kg/mol)	I_s (sec)		k
		By Mass	By Volume					Shifting	Frozen	
Oxygen	Methane	3.20	1.19	0.81	3526	1835			296	
		3.00	1.11	0.80	3526	1853		311		
	Hydrazine	0.74	0.66	1.06	3285	1871	18.3		301	1.25
		0.90	0.80	1.07	3404	1892	19.3	313		
	Hydrogen	3.40	0.21	0.26	2959	2428	8.9		386	1.26
		4.02	0.25	0.28	2999	2432	10.0	389.5		
	RP-1	2.24	1.59	1.01	3571	1774	21.9	285.4		1.24
		2.56	1.82	1.02	3677	1800	23.3		300	
	UDMH	1.39	0.96	0.96	3542	1835	19.8		295	1.25
		1.65	1.14	0.98	3594	1864	21.3	310		
Fluorine	Hydrazine	1.83	1.22	1.29	4553	2128	18.5	334		1.33
		2.30	1.54	1.31	4713	2208	19.4		365	
	Hydrogen	4.54	0.21	0.33	3080	2534	8.9		389	1.33
		7.60	0.35	0.45	3900	2549	11.8	410		
Nitrogen tetroxide	Hydrazine	1.08	0.75	1.20	3258	1765	19.5		283	1.26
		1.34	0.93	1.22	3152	1782	20.9	292		
	50% UDMH–	1.62	1.01	1.18	3242	1652	21.0		278	1.24
	50% hydrazine	2.00	1.24	1.21	3372	1711	22.6	289		
	RP-1	3.4	1.05	1.23	3290		24.1		297	1.23
		2.15	1.30	1.20	3396	1747	22.3	289		
	MMH	1.65	1.00	1.16	3200	1591	21.7		278	1.23
Red fuming nitric acid		4.1	2.12	1.35	3175	1594	24.6		258	1.22
	4.8	2.48	1.33	3230	1609	25.8	269			
50% UDMH–	1.73	1.00	1.23	2997	1682	20.6		272	1.22	
50% hydrazine	2.20	1.26	1.27	3172	1701	22.4	279			
Hydrogen peroxide (90%)	RP-1	7.0	4.01	1.29	2760		21.7		297	1.19

Notes:

Combustion chamber pressure—1000 psia (6895 kN/m²); nozzle exit pressure—14.7 psia (1 atm); optimum expansion.

Adiabatic combustion and isentropic expansion of ideal gas

The specific gravity at the boiling point was used for those oxidizers or fuels that boil below 20°C at 1 atm pressure.

Mixture ratios are for approximate maximum value of I_s .

Source: Sutton, *Rocket Propulsion Elements*

Rocket Performance Tools

Chemical Equilibrium with Applications (CEA)

- Free but must request online at <https://software.nasa.gov/software/LEW-17687-1>
- New requirements around distribution that make it difficult to use

pypropep

- Python wrapper around C-port of an old Fortran code!
- Works well and has a large propellant database included
- No advanced features (finite area contraction for instance)
- Requires some basic Python knowledge

Rocket Propulsion Analysis (RPA)

- Commercial GUI application for Windows/Mac
- Free version that will do basic equilibrium rocket calculations
- Probably easiest entry point all things considered

Trends and Takeaways
