Climate Change Reversal Using Sodium as an Aircraft Fuel Additive

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Opportunity:

Can we develop an aviation fuel additive that reverses climate change using Stratospheric Aerosol Injection (SAI)?

We need an alternative fuel system that is:

- Readily produced by solar energy
- Burned efficiently to release energy
- Creates an exhaust free of carbon dioxide
- Results in reduced solar energy absorption to the atmosphere

The answer may be sodium! (Ref. 1)

"Wicked-Wild" Idea:

Sodium burned with hydrocarbon fuel, for example methane, will produce sodium carbonate:

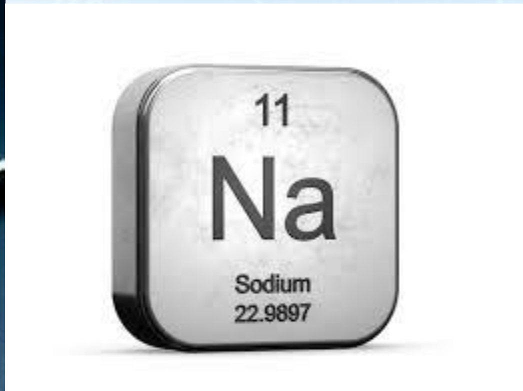
$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)}\ (\Delta H = -50\ \mathrm{MJ/kg})$$

$$\mathrm{2CH_4(g) + 4Na(s) + 5CO_2(g) \rightarrow 2Na_2CO_3}(s)\ \mathrm{+ 4H_2O(g)}\ (\Delta H = -25\ \mathrm{MJ/kg})$$

The energy density of sodium, while less than that of hydrocarbons, is still very high. The sodium carbonate released will be a fine aerosol. If released high enough in the atmosphere, this will reduce absorption of sunlight in the atmosphere. Additionally, sodium carbonate is alkaline and if absorbed in the ocean, could reduce acidification.

DV&F Challenges:

- As a highly reactive metal, how can sodium be stored, transported, and fueled in an aircraft?
- How can sodium be efficiently burned in an aircraft engine?
- Can we accept the lower fuel energy density that the addition of sodium in the fuel presents?
- How can we assure that the sodium carbonate produced does not contaminate areas where humans reside (burn only over oceans)?
- Will society accept "geoengineering" as a means to reverse climate change?



Geoengineering and Stratospheric Atmospheric Injection Background

- Geoengineering is the large-scale, intentional changes to the Earth's environment to reduce the effects of climate change.
- Solar radiation management (SRM) or albedo modification is a type of geoengineering that reflects sunlight back into space to cool the planet.
- NASA and the Federal Government through the National Academies of Science have participated in Solar Geoengineering Research and Research Governance (Ref 2 through 4), but most of the NASA aeronautic research programs have not worked in solar geoengineering.
- One possible implementation of SRM is stratospheric atmospheric injection (SAI) where particle are released in the upper atmosphere from aircraft.
- Other aeronautical activities have investigated the use of aircraft for solar geoengineering, but the work has not yet generated widespread acceptance (Ref. 5 through 8).

Reaction Stoichiometry - I

Consider burning sodium with hydrocarbon fuel:

$$2\ C_nH_{2n+2} + (3n+1)\ O_2\ \rightarrow 2n\ CO_2 + 2(n+1)\ H_2O$$

$$2\ Na + CO_2 + \frac{1}{2} O_2 \rightarrow Na_2CO_3$$

$$4n\ Na + 2n\ CO_2 + n\ O_2 \rightarrow 2n\ Na_2CO_3$$

$$\boxed{2\ C_nH_{2n+2} + 4n\ Na + (4n+1)\ O_2\ \rightarrow 2n\ Na_2CO_3 + 2(n+1)\ H_2O}$$

Reaction Stoichiometry - II

Assume aviation fuel is dodecane $C_{12}H_{26}$ $(n = 12)$

Combustion in Oxygen

$$2\ C_{12}H_{26} + 48\ Na + 49\ O_2 \ \rightarrow 24\ Na_2CO_3 + 26\ H_2O$$

Combustion in Air (21% O_2 & 79% N_2 by mole)

$$2\ C_{12}H_{26} + 48\ Na + 49\ O_2 + \frac{79}{21} 49\ N_2 \rightarrow 24\ Na_2CO_3 + 26\ H_2O + \frac{79}{21} 49\ N_2$$

$$2\ C_{12}H_{26} + 48\ Na + 49\ O_2 + 184.3\ N_2 \rightarrow 24\ Na_2CO_3 + 26\ H_2O + 184.3\ N_2$$

Reaction Stoichiometry - III

MW H = 1.008 g/mol

MW N = 14.0067 g/mol

MW O =15.994 g/mol

MW Na = 22.9898 g/mol

MW O_2 = $2 \cdot 15.9994$ = 31.9988 g/mol

MW N_2 = $2 \cdot 14.0067$ = 28.0134 g/mol

MW Dodecane = $12 \cdot 12.011 + 26 \cdot 1.008$ = 170.34 g/mol

MW Air = $0.21 \cdot 2 \cdot 15.9994 + 0.79 \cdot 2 \cdot 14.0067$ = 28.8503 g/mol

Reaction Stoichiometry - IV

$$2\ C_{12}H_{26} + 48\ Na + 49\ O_2 + \frac{79}{21} 49\ N_2 \rightarrow 24\ Na_2CO_3 + 26\ H_2O + \frac{79}{21} 49\ N_2$$

Mass Dodecane = 2 · 170.34 = 340.68 g

Mass Sodium = 48 · 22.989769 = 1103.51 g

Mass Dodecane Air = (24 + 13) · (31.9988 + 79/21 · 28.0134) = 5083.2 g

Mass Sodium Air = 12 · (31.9988 + 79/21 · 28.0134) = 1648.6 g

Mass Total Air = 49 · (31.9988 + 79/21 · 28.0134) = 6731.7 g

Mass sodium to mass of dodecane = 1103.51 / 340.68 = 3.239

Mass total air to mass of dodecane = 6731.7 / 340.68 = 19.76

Mass total air to mass of sodium = 6731.7 / 1103.51 = 6.100

Mass total air to mass of fuel (dodecane + sodium)

= 6730.8 / (1103.51 + 340.68) = 4.661

Equilibrium Calculations

- Use the Aerotherm Chemical Equilibrium code (Ref 9.) to compute the gas composition and conditions for sodium carbonate particulate formation
- Code uses thermodynamic data from the 1992 JANNAF thermochemical Tables (ref 10.).
- Conditions computed for various amount of sodium in the combustion stream.
- Code also allows the flame temperature to be computed given the standard heats of formation for the reactants.

Heat of Combustion - I

For stoichiometric combustion:

Dodecane plus sodium:

$$2\ \mathrm{C_{12}H_{26}(l)} + 48\ \mathrm{Na(s)} + 49\ \mathrm{O_2(g)} \rightarrow 24\ \mathrm{Na_2CO_3(s)} + 26\ \mathrm{H_2O(g)}$$

ΔH_c= ½ (24 · (-1130.8) + 26 · (-241.8) - 2 · (-352.1)) = -16,360 J/mol

= -22.66 J/g of fuel (dodecane + sodium)

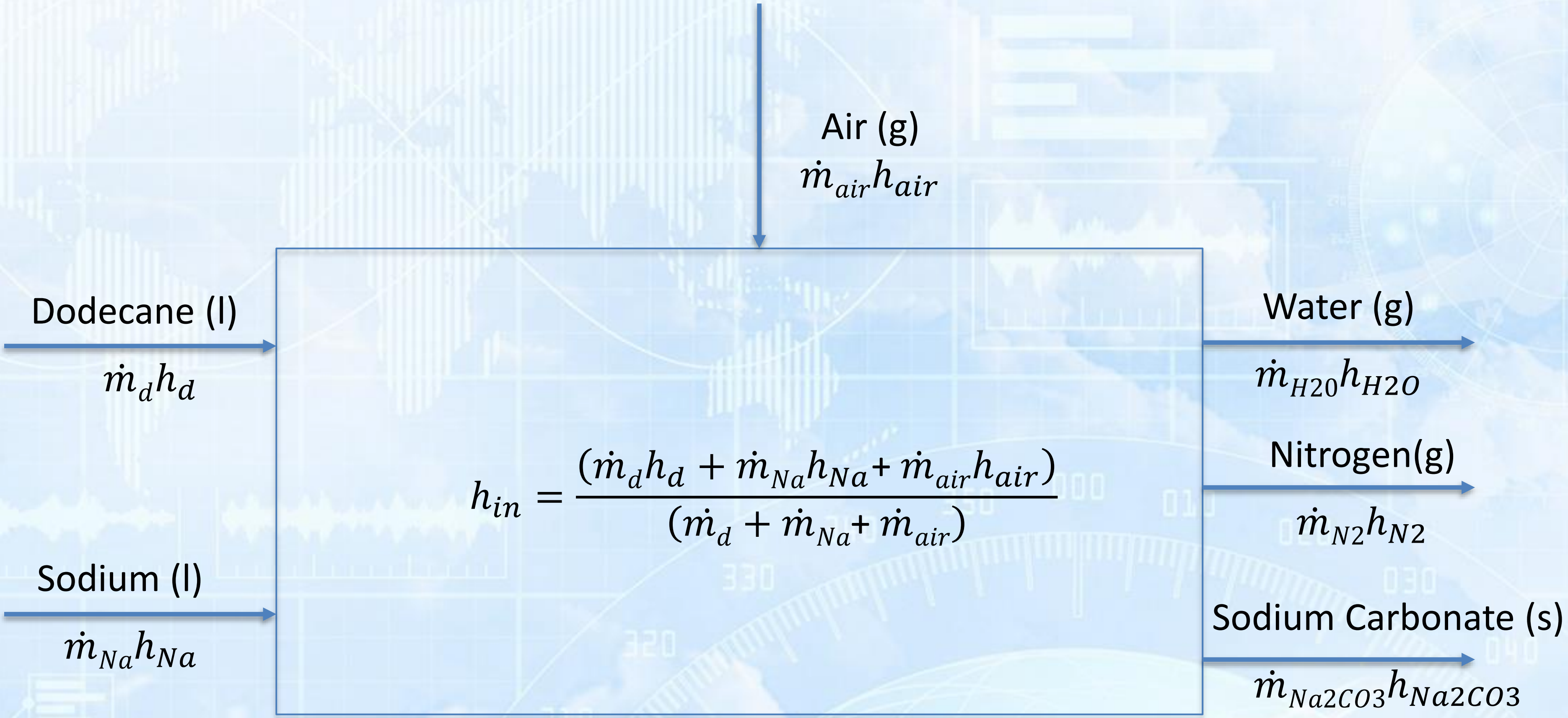
Dodecane alone:

$$2\ \mathrm{C_{12}H_{26}(l)} + 37\ \mathrm{O_2(g)} \rightarrow 24\ \mathrm{CO_2(g)} + 26\ \mathrm{H_2O(g)}$$

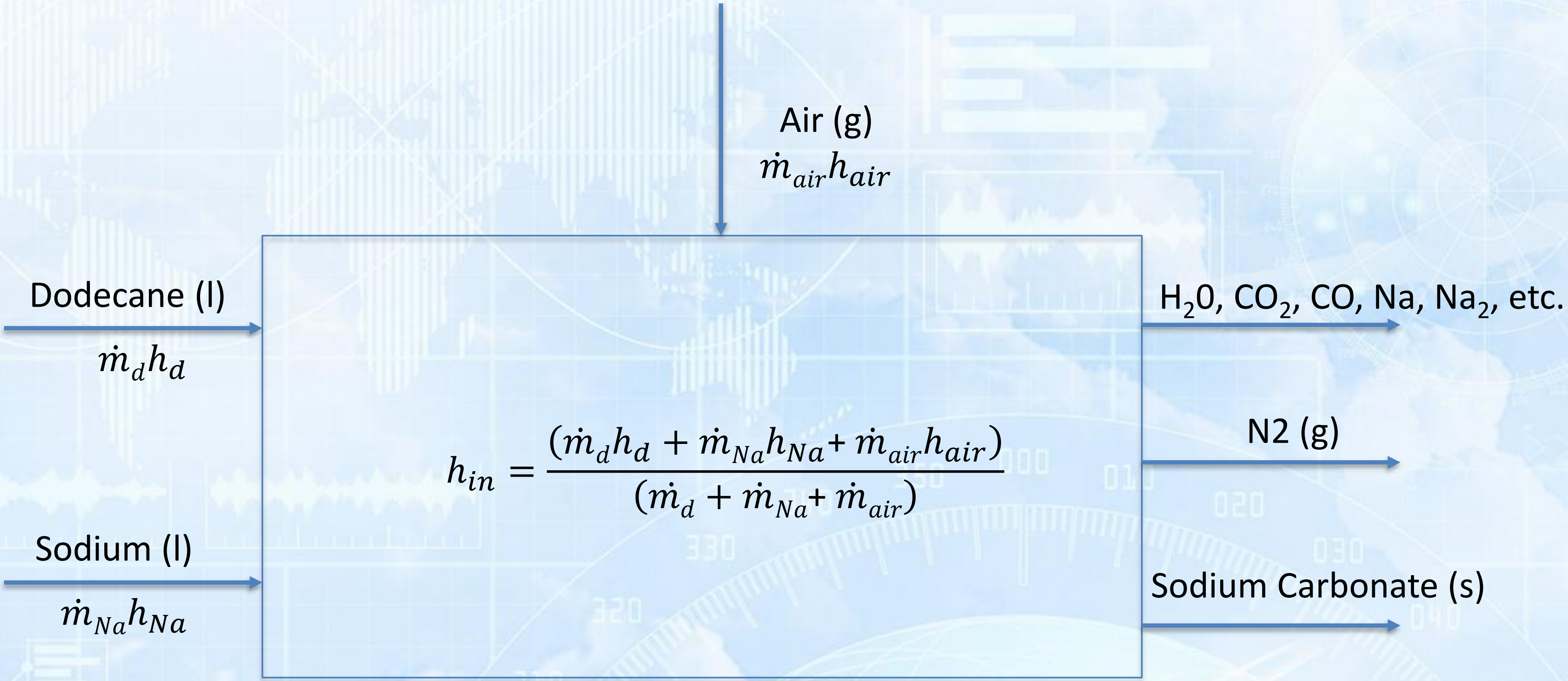
ΔH_c= ½ (24 · (-393.5) + 26 · (-241.8) – 2 · (-352.1)) = -7,513.9 J/mol

= -44.11 J/g of fuel (dodecane)

Ideal Combustion



RealCombustion



Heat of Formation Values

Component	Hf (kJ/mol)	MW (g/mol)	Hf (J/g)	Heat of Formation Source
O_2 (g)	0	31.9988	0.00	By definition
N_2 (g)	0	28.0134	0.00	By definition
Ar (g)	0	39.948	0.00	By definition
CH_6 (g)	-74.87	16.043	-4666.83	https://webbook.nist.gov/cgi/cbook.cgi?ID=C74828&Units=SI&Mask=1#Thermo-Gas
$C_{12}H_{26}$ (l)	-352.1	170.34	-2067.04	https://webbook.nist.gov/cgi/cbook.cgi?ID=C112403&Mask=2#Thermo-Condensed
Na (s)	0	22.989769	0.00	https://janaf.nist.gov/tables/Na-001.html
Na (l)	2.406	22.989769	104.66	https://janaf.nist.gov/tables/Na-003.html
Na (g)	107.3	22.989769	4667.29	https://janaf.nist.gov/tables/Na-005.html
CO_2 (g)	-393.522	44.0098	-8941.69	https://janaf.nist.gov/tables/C-095.html
H_2O (g)	-241.826	18.0154	-13423.29	https://janaf.nist.gov/tables/H-064.html
H_2O (l)	-285.830	18.0154	-15865.87	https://janaf.nist.gov/tables/H-063.html
Na_2O (s)	-417.982	61.978938	-6743.94	https://janaf.nist.gov/tables/Na-012.html
Na_2CO_3 (s)	-1130.768	105.988738	-10668.76	https://janaf.nist.gov/tables/C-090.html
Air (mole)	0.00	29.0999	0.00	By definition

Equivalence Sodium Mass Ratio

Assume ratio of dodecane to air is fixed but vary the amount of sodium. The amount of air is set to stoichiometric ratio of complete sodium and dodecane combustion to sodium carbonate assuming stoichiometric sodium ($\dot{m}_{air}/\dot{m}_d$ = 19.76).

Define the equivalence sodium mass ratio as the actual ratio of mass of sodium to mass of dodecane over the stoichiometric ratio of mass of sodium to mass of dodecane and providing stoichiometric air for both dodecane and sodium.

For example, the stoichiometric mass ratio of sodium to dodecane is 3.239 to 1, so for an equivalence ratio of 1, we would have 1 part dodecane by mass, 3.239 parts sodium, and 19.76 parts air. For an equivalence ratio of 3, then we would have 1 part dodecane by mass and $3 \cdot 3.239$ or 9.717 parts sodium and 19.76 parts air.

Adiabatic Flame Temperature Initial Conditions

Determine net heat of formation for reactants. Define the stoichiometric ratio of sodium Φ as the actual amount of sodium versus stoichiometric sodium (by mass)

$$\text{Reactants} = 1 \text{ part dodecane} + 3.239 \cdot \Phi \text{ parts sodium} + 19.76 \text{ parts air}$$

$$\text{Heat of formation} = (\text{-}2067.04 + 3.239 \cdot \Phi \cdot 104.66 + 19.76 \cdot 0)$$
$$/(1 + 3.239 \cdot \Phi + 19.76) \text{ J/g}$$

For $\Phi = 1$

$$\text{Heat of formation} = (\text{-}2067.04 + 3.239 \cdot 104.66 + 19.76 \cdot 0)$$
$$/(1 + 3.239 + 19.76) = \text{-}72.00 \text{ J/g} = \text{-}17.21 \text{ cal/g}$$

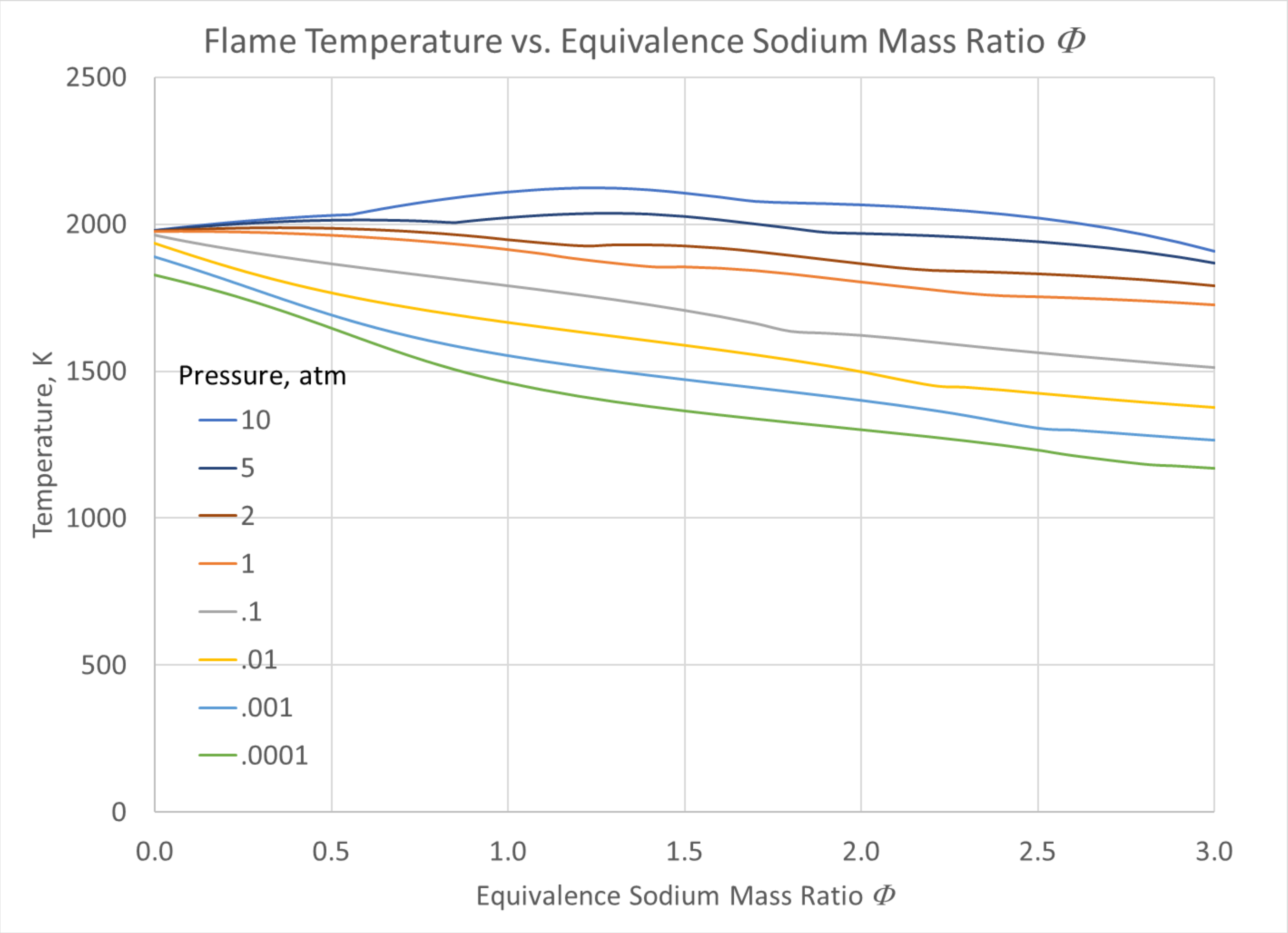
Thermochemical Equilibrium Calculations

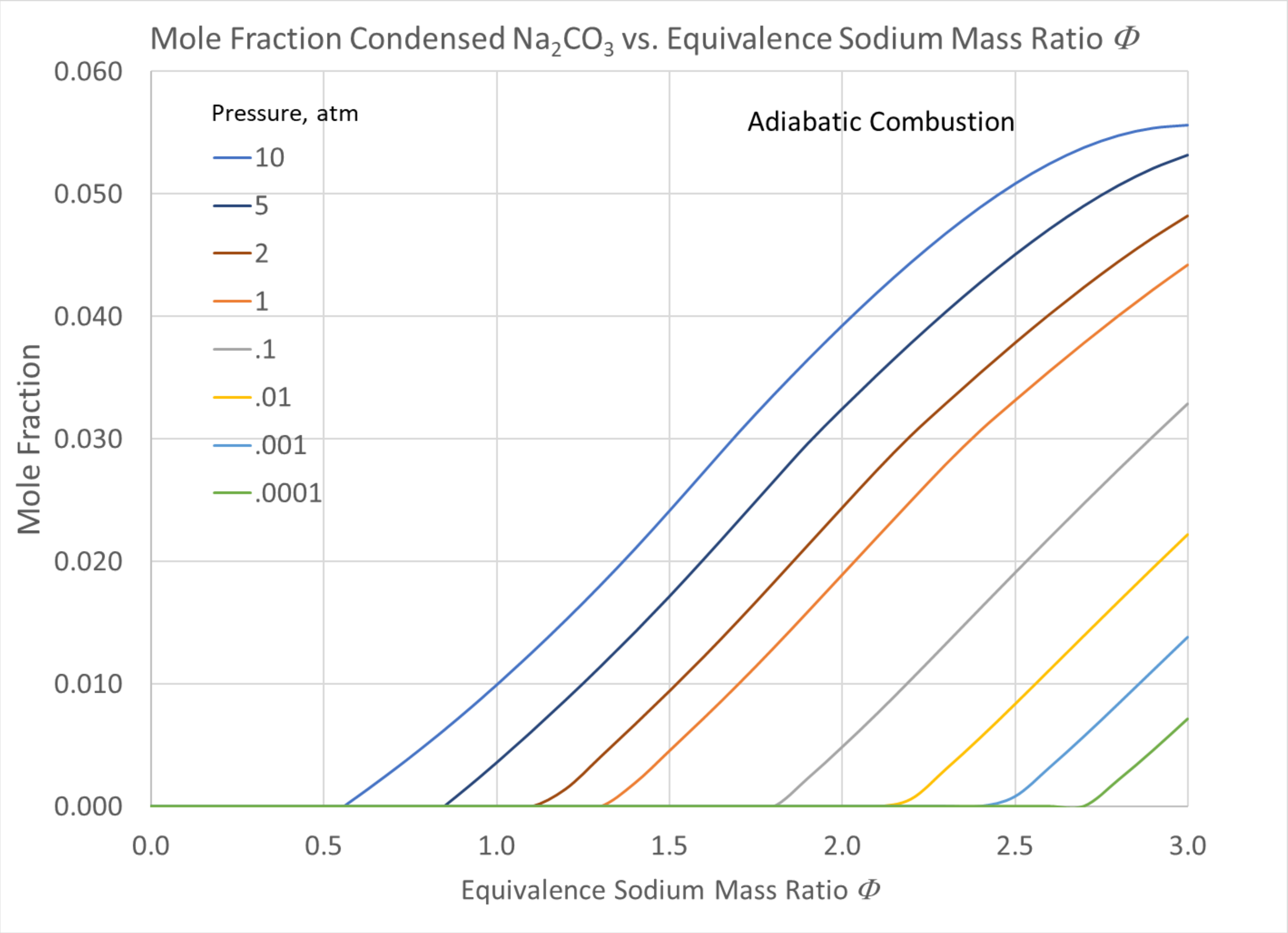
Gas Phase Species Included

H2O1(g) , C1O1(g) , C1O2(g), N2(ref), H1Na1O1(g), Ar1(ref), C1(g) , C1H1(g), C1H1N1(g), C1H1N1O1(g), C1H1O1(g), C1H2(g), C1H2O1(g), C1H3(g) , C1H4(g) , C1N1(g) , C1N1Na1(g), C1N1O1(g), C1N2(g), C2(g) , C2H1(g), C2H2(g), C2H4(g), C2H4O1(g), C2N1(g), C2N2(g), C2N2Na2(g), C2O1(g), C3(g), C3O2(g), C4(g), C4N2(g), C5(g), H1(g), H1N1(g), H1N1O1(g), H1N1O2(g), H1N1O2(g)H1N1O3(g), H1Na1(g), H1O1(g), H1O2(g), H2(ref), H2N1(g), H2N2(g), H2Na2O2(g), H2O2(g), H3N1(g), H4N2(g), N1(g), N1O1(g), N1O2(g), N1O3(g), N2O1(g), N2O3(g), N2O4(g), N2O5(g), N3(g), Na1(g), Na1O1(g), Na2(g), O1(g), O2(ref), O3(g)

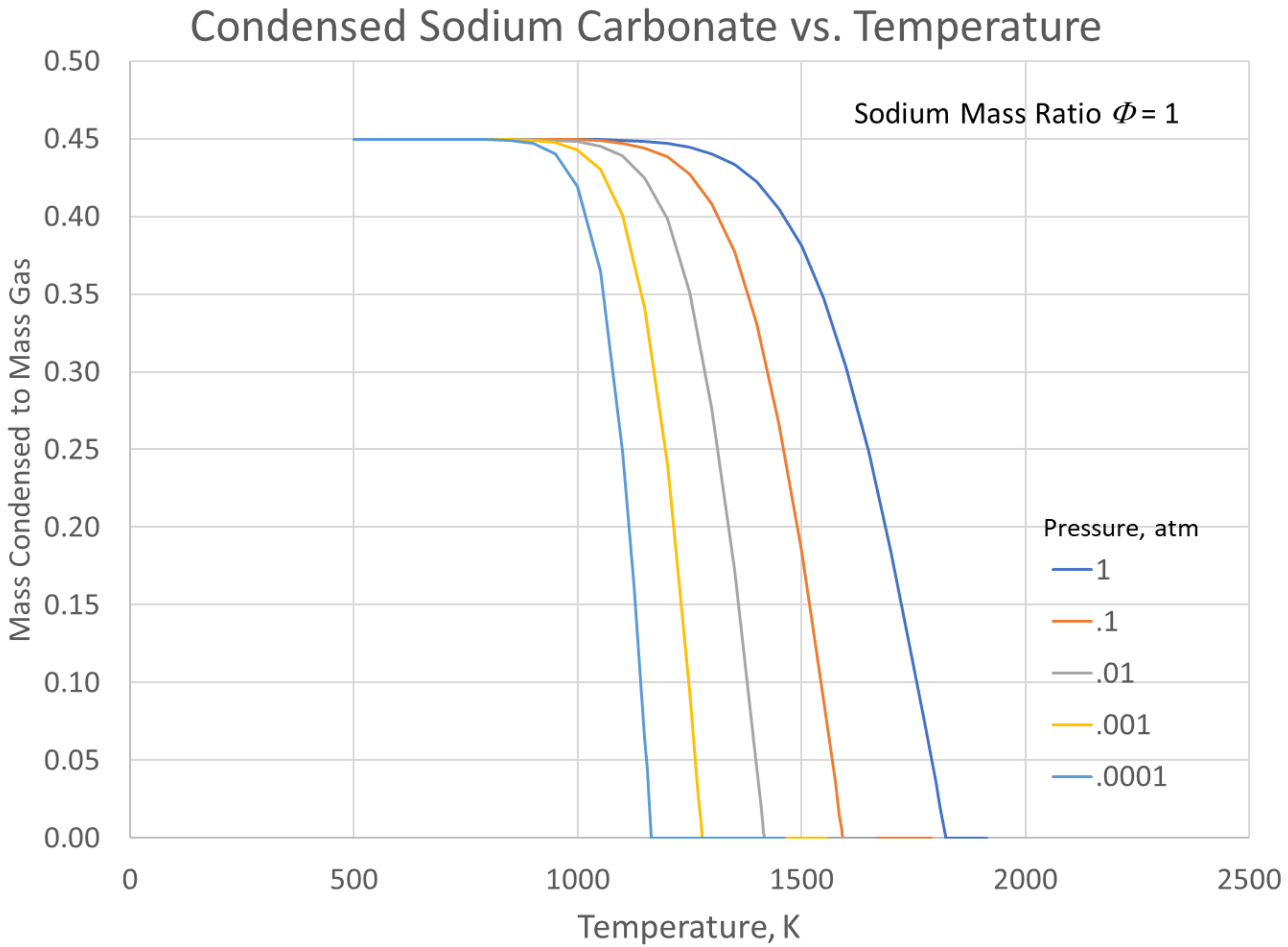
Condensed Phase Species Included

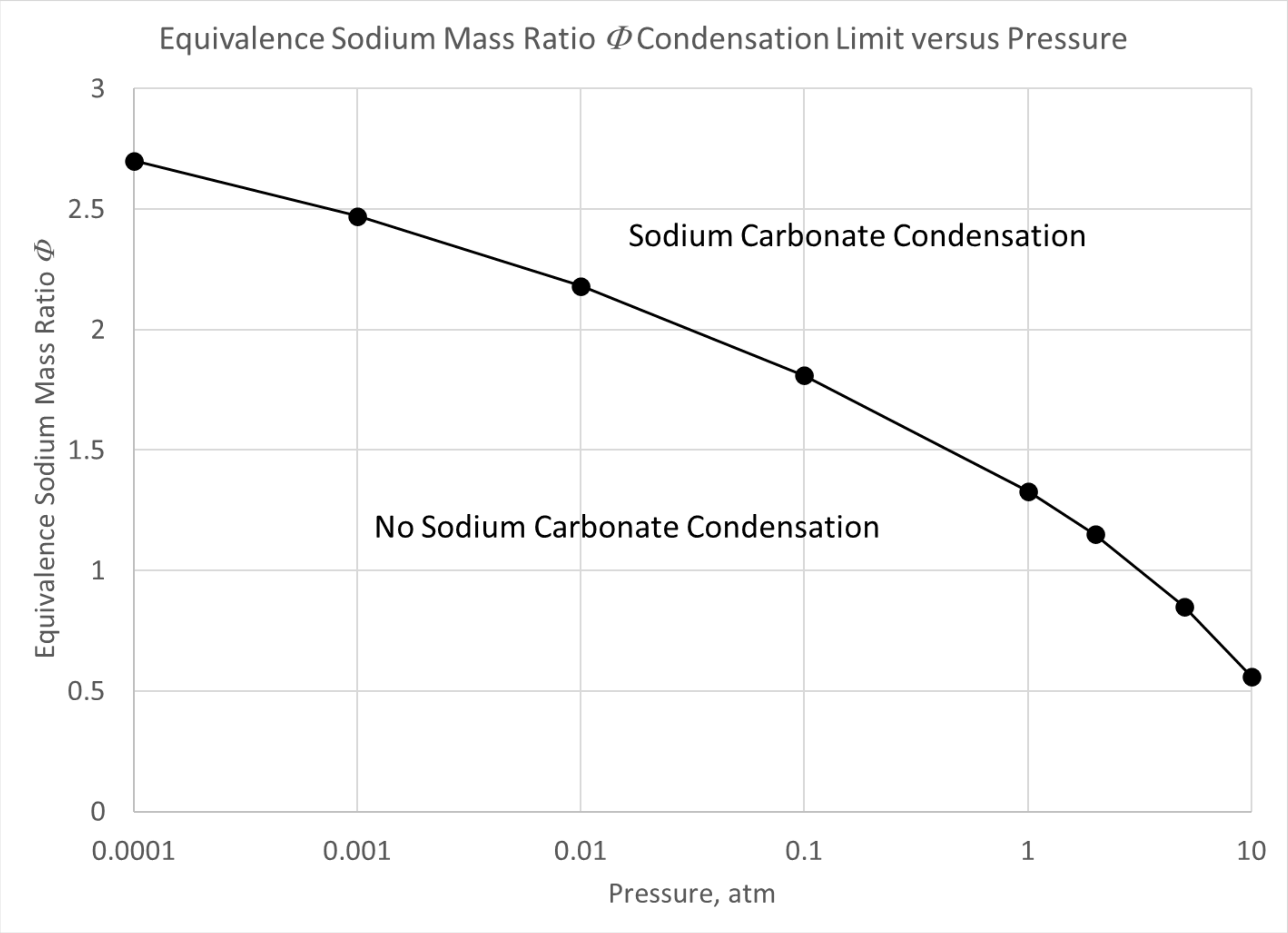
C1N1Na1*, C1Na2O3*, Na1*, Na2O1*

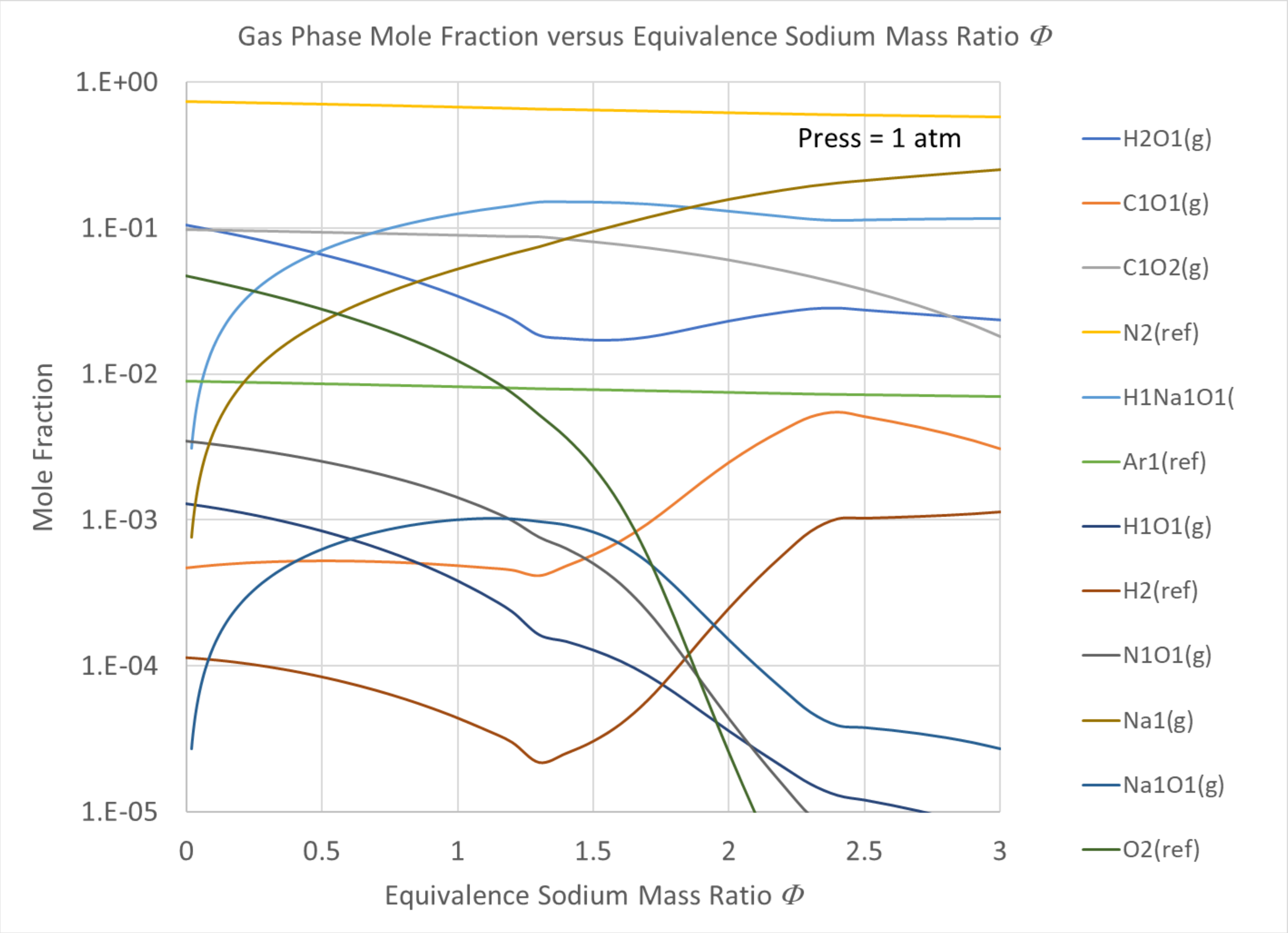

Flame Temperature vs. Equivalence Sodium Mass Ratio Φ
2500
2000
1500
1000
500
0
Temperature, K
Pressure, atm
10
5
2
1
.1
.01
.001
.0001
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Equivalence Sodium Mass Ratio Φ



Mole Fraction Condensed Na_2CO_3 vs. Equivalence Sodium Mass Ratio Φ
Pressure, atm
10
5
2
1
.1
.01
.001
.0001
Adiabatic Combustion
Mole Fraction
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Equivalence Sodium Mass Ratio Φ


Condensed Sodium Carbonate vs. Temperature
Sodium Mass Ratio Φ = 1
Mass Condensed to Mass Gas
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
500
1000
1500
2000
2500
Temperature, K
Pressure, atm
1
.1
.01
.001
.0001


Equivalence Sodium Mass Ratio Φ Condensation Limit versus Pressure
Sodium Carbonate Condensation
No Sodium Carbonate Condensation
Equivalence Sodium Mass Ratio Φ
Pressure, atm
0
0.5
1
1.5
2
2.5
3
0.0001
0.001
0.01
0.1
1
10



Gas Phase Mole Fraction versus Equivalence Sodium Mass Ratio Φ
Press = 1 atm
Mole Fraction
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
0
0.5
1
1.5
2
2.5
3
Equivalence Sodium Mass Ratio Φ
H2O1(g)
C1O1(g)
C1O2(g)
N2(ref)
H1Na1O1(
Ar1(ref)
H1O1(g)
H2(ref)
N1O1(g)
Na1(g)
Na1O1(g)
O2(ref)

Thermochemical Results

- The flame temperature of dodecane alone is generally higher than that of dodecane and sodium because of the higher heat of combustion of dodecane alone.
- Sodium carbonate is the only observed condensed phase in the combustion of dodecane and sodium based upon thermodynamic equilibrium.
- For adiabatic combustion, the higher the ratio of sodium to dodecane, the greater amount of sodium carbonate produced.
- Under adiabatic conditions, combustion at higher pressures produces more sodium carbonate than at lower pressures.
- Sodium carbonate condenses art lower temperatures under higher pressures.
- For combustion pressures greater than about 3 atm, sodium level must be below the stoichiometric ratio to prevent formation of sodium carbonate.

Sodium Carbonate Safety

- Sodium carbonate presents a potential environmental hazard due to its potential health hazard and is classified as a "health level 2 chemical."
- A "health level 2 chemical" refers to a substance that poses a moderate health hazard, meaning it can cause skin irritation, eye irritation, or reversible eye injury, but not severe or life-threatening effects.

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.12.2014 Page 2 of 7

Sodium Carbonate,Anhydrous

NFPA/HMIS

NFPA SCALE (0-4)

Health	2
Flammability	0
Physical Hazard	0
Personal Protection	X

HMIS RATINGS (0-4)

SECTION 2 : Hazards identification

Classification of the substance or mixture:

Irritant
Eye irritation, category 2A

Eye Irritation 2

Signal word :Warning

Hazard statements:
Causes serious eye irritation
Precautionary statements:
If medical advice is needed, have product container or label at hand
Keep out of reach of children
Read label before use
Do not eat, drink or smoke when using this product
Wear protective gloves/protective clothing/eye protection/face protection
Wash skin thoroughly after handling
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do.
Continue rinsing
If eye irritation persists get medical advice/attention

Required Future Work

- Need to evaluate scattering cross section of sodium carbonate particles to determine solar scattering effectiveness
- No sources for complex index of refraction found in literature
  - Index of refraction
  - Extinction coefficient
- Consider experimentally measuring complex index of refraction
- Ultimately use Mie theory to calculate particle size to give maximum backscatter for given wavelengths

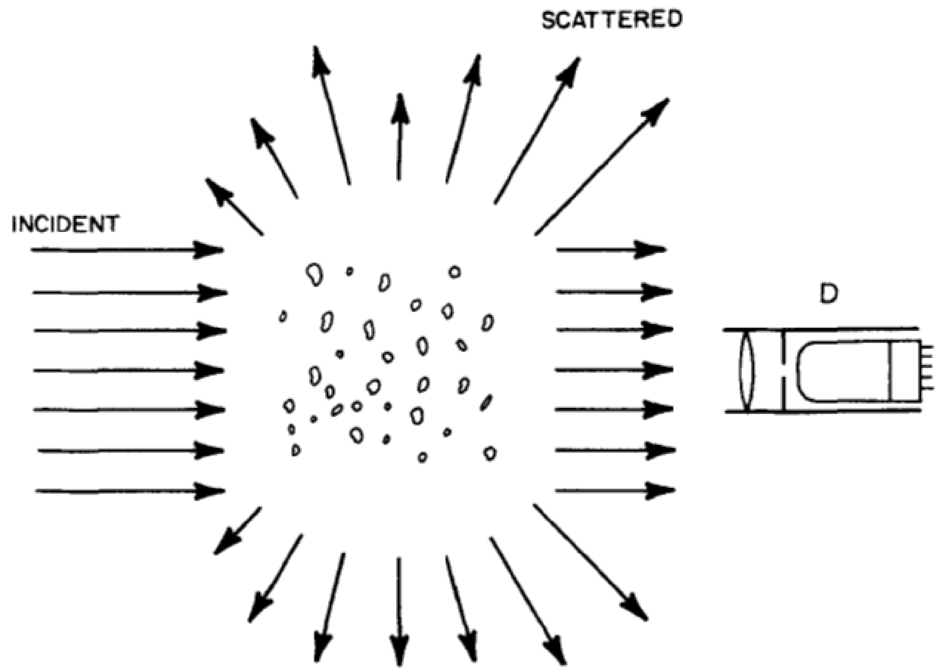


Figure 3.6 Extinction by a collection of particles.

Summary of Current Work

- Computed equilibrium combustion chemistry to identify conditions (fuel/air ratio) where the method is feasible and determine quantity of sodium carbonate that can be produced
- Determined energy content of sodium combustion with aviation fuel
- Further research current U.S./NASA efforts in Stratospheric Aerosol Injection (SAI)
- Contacted U.S. academic expert on SAI
  - Not familiar with concept and could not evaluate feasibility of concept
- Performed preliminary evaluation of sodium carbonate toxicology and identified this as a potential barrier (NFPA Health 2)

Path Forward

- Determine NASA's current role in Stratospheric Aerosol Injection (SAI) and Identify groups in NASA with experience in climate change due to aerosols and clouds
- Locate in literature or measure complex index of refraction (index of refraction and extinction coefficient) for sodium carbonate
- Compute scattering cross section of sodium carbonate particles and determine required particle sizes to optimally reflect sunlight
- Further evaluate toxicology of sodium carbonate
- Identify possible propulsion concepts capable of burning sodium

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