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Nomenclature

		F	Helmholtz free-energy
\hat{R}	Universal gas constant ≈ 8314 kJ/kg-K	G	Gibbs free-energy
λ	Lagrange multiplier	h'	Sum of contributions from each species towards enthalpy constraint, i.g. $\sum_j^{\text{NS}} \mathcal{N}_j H_j^\circ$
\mathcal{L}	The Lagrangian	h'_0	User-specified enthalpy (J/kg)
\mathcal{N}	Total kg-moles per unit mass in the system	H_j°	Standard state enthalpy of species j (J/kg)
\mathcal{N}_j	Number of kg-moles per unit mass of species j in the system	MW_j	Molecular weight of species j in kg / kg-mole
μ_j	Chemical potential of species j	p_{ref}	Reference temperature used to compute chemical potential
μ_j°	Standard state chemical potential of species j	q_j	Charge of species j (0 for neutrals, 1 for ions, -1 for electrons)
ρ	Density (kg/m^3)	T	Temperature (K)
a_{ij}	Stoichiometric coefficients, e.g. number of atoms of element i in species j . Weighted by element i 's molecular weight	u'	Sum of contributions from each species towards internal energy constraint, i.g. $\sum_j^{\text{NS}} \mathcal{N}_j U_j^\circ$
b_i	Sum of contributions from each species towards constraint for element i , i.g. $\sum_{j=1}^{\text{NS}} a_{i,j} \mathcal{N}_j$	u'_0	User-specified internal energy (J/kg)
b_i°	Specified number of moles of element i	U_j°	Standard state internal energy of species j (J/kg)
$c_{p,j}^\circ$	Standard state specific heat of species j	V	Specific volume (m^3/kg)
$c_{v,j}^\circ$	Standard state specific heat of species j		

1 Minimization Procedures

1.1 Constraints for Both Procedures

There are two constraints that are used the most in both energy minimization procedures. The first, equation [1.1], is always used, while the charge constraints in equation [1.2] is only used when ions are present:

$$\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j - b_i^{\circ} = 0 \quad (1.1)$$

$$\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j = 0 \quad (1.2)$$

Since these are used in abundance for both procedures, their constraints are placed in the Lagrangian term. Other constraints (such as specified volume, temperature, internal energy, and entropy) are given their own residual equations in the Newton solve without addition into the Lagrangian.

Equation [1.1] says that the number of moles of element i must remain constant during the minimization process, as atoms can not be created or destroyed without nuclear reactions being involved. b_i° is the number of moles of element i before minimizing, and a_{ij} is the stoichiometric coefficient, i.e. how many atoms of element i are in species j . In this code, the stoichiometric coefficient is actually multiplied by the element's molecular weight. The current reason is not known, though it needs to be figured out why this method yields correct results.

Equation [1.2] says that the charge of the system must remain neutral, i.e., if cations are formed, then there must be an equal number of free electrons in the gas to balance the charge.

1.2 The Lagrangian

The Lagrangian is defined as;

$$\mathcal{L} = f + \sum_j \lambda_j g_j \quad (1.3)$$

where f is the function we want to minimize, λ_j are Lagrange multipliers, and

g_j are the constraint functions equal to 0. Instead of minimizing just f , we aim to minimize the Lagrangian \mathcal{L} .

1.3 Newton-Raphson Iterative Method

A Newton-Raphson iterative procedure is used to minimize the energies. Since this is essentially a root finding system of equations, and we are seeking the solution update, the method looks like the following after using a Taylor expansion on the function f :

$$\sum_{i=1}^N \frac{\partial f}{\partial x_i} \Delta x_i = -f(x) \quad (1.4)$$

Here, $f(x)$ is the function that is being minimized. In the case of Gibbs and Helmholtz energy minimization, f takes the form of $\partial \mathcal{L} / \partial x$, with x being non-linear variables used to guide the convergence of the system. The non-linear correction variables are in the form of $\Delta \ln \mathcal{N}_j$, $\Delta \ln \mathcal{N}$, $\Delta \ln T$, and $\pi_{i,q} = \Delta \pi_{i,q}$. For the last correction variable, it is argued that setting π to 0 at the beginning of each update does not influence the solution for the non-reduced equations, so the Δ is dropped for that term. This will influence the form of the update equations, which will be talked about in due time.

1.4 Gibbs Minimization

The Gibbs energy is a function of temperature, pressure, and composition of a gas:

$$G = G(T, p, \mathcal{N}_1, \mathcal{N}_2, \dots, \mathcal{N}_{\text{NS}}) = \sum_{j=1}^{\text{NS}} \mathcal{N}_j \mu_j \quad (1.5)$$

Where NS is the number of gas species, \mathcal{N}_j is the number of kg-moles of species j per kilogram (i.e., the mole-mass fraction), and μ_j is the chemical potential of species j defined by:

$$\mu_j = \frac{\partial G}{\partial \mathcal{N}_j} = \mu_j^\circ + \hat{R}T \left[\ln \left(\frac{p}{p_{\text{ref}}} \right) + \ln \left(\frac{\mathcal{N}_j}{\mathcal{N}} \right) \right] \quad (1.6)$$

Here, \hat{R} is the universal gas constant, T and p are the temperature and pressure of the system, p_{ref} is the reference pressure (usually takes as 101,325 Pa, or 1 bar depending on the literature), and \mathcal{N} is the number of kg-moles

per unit mass in the system. In order to find chemical equilibrium, the derivative of G wrt \mathcal{N}_j is set to 0 for all species. However, a number of constraints need to be added in.

1.4.1 Constraints

Firstly, the elemental constraint from equation [1.1] is added into the Lagrangian for our Gibbs function. If ions are present, the charge constraint [1.2] is also put in. Therefore, our Lagrangian is:

$$\mathcal{L} = \sum_{j=1}^{\text{NS}} \mu_j \mathcal{N}_j + \sum_{i=1}^{\text{NE}} \lambda_i \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j - b_i^{\circ} \right] + \lambda_q \left[\sum_{j=0}^{\text{NS}} q_j \mathcal{N}_j \right] \quad (1.7)$$

The constraints available for the Gibbs energy are:

- Hold temperature (T) and pressure (P) constant.
- Hold enthalpy (H) and pressure (P) constant.
- Hold entropy (S) and pressure (P) constant.

For all Gibbs minimizations, we need the molar constraint:

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j - \mathcal{N} = 0 \quad (1.8)$$

For (TP) minimization, only the elemental and charge (if present) constraints are necessary. For (HP) minimization, the constraint is defined by:

$$h' - h'_0 = 0 \quad (1.9)$$

Where h'_0 is the specified enthalpy in J/kg, and h' is solved for during the minimization process as:

$$h' = \sum_{j=1}^{\text{NS}} \mathcal{N}_j H_j^{\circ} \quad (1.10)$$

For (SP) minimization, the constraint is defined by:

$$s' - s'_0 = 0 \quad (1.11)$$

Where s'_0 is the specified entropy and s' is solved for in the minimization process as:

$$s' = \sum_{j=1}^{\text{NS}} \mathcal{N}_j S_j \quad (1.12)$$

where:

$$S_j = S_j^\circ - \hat{R} \ln \frac{\mathcal{N}_j}{\mathcal{N}} - \hat{R} \ln p \quad (1.13)$$

1.4.2 Derivatives

We now take the derivatives of \mathcal{L} wrt \mathcal{N}_j , and each λ and denote them as f :

$$f_1 = \frac{\partial \mathcal{L}}{\partial \mathcal{N}_j} = \mu_j + \sum_{i=1}^{\text{NE}} \lambda_i a_{ij} + \lambda_q q_j = 0 \quad (1.14)$$

$$f_2 = \frac{\partial \mathcal{L}}{\partial \lambda_i} = \sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j - b_i = 0 \quad (1.15)$$

$$f_3 = \frac{\partial \mathcal{L}}{\partial \lambda_q} = \sum_{j=0}^{\text{NS}} q_j \mathcal{N}_j = 0 \quad (1.16)$$

These three equations are our minimization functions. Through use of the aforementioned Newton-Raphson method, we can solve these equations. Additional residual equations for total moles of the system, enthalpy, and entropy are:

$$f_4 = \sum_{j=1}^{\text{NS}} \mathcal{N}_j - \mathcal{N} = 0 \quad (1.17)$$

$$f_5 = \frac{h' - h'_0}{\hat{R}T} = \frac{\sum_{j=1}^{\text{NS}} \mathcal{N}_j H_j^\circ - h'_0}{\hat{R}T} \quad (1.18)$$

$$f_6 = \frac{s' - s'_0}{\hat{R}} = \frac{\sum_{j=1}^{\text{NS}} \mathcal{N}_j S_j - s'_0}{\hat{R}} \quad (1.19)$$

Special care needs to be taken in the enthalpy constraint to include the enalpies of formation and/or reference enthalpies, if applicable.

1.4.3 Derivatives of f_1

First, we must do some algebraic manipulation. We start by expanding equation [1.14] with equation [1.6]:

$$\frac{\partial \mathcal{L}}{\partial \mathcal{N}_j} = \mu_j^\circ + \hat{R}T \left[\ln \left(\frac{p}{p_{\text{ref}}} \right) + \ln \left(\frac{\mathcal{N}_j}{\mathcal{N}} \right) \right] + \sum_{i=1}^{\text{NE}} \lambda_i a_{ij} + \lambda_q q_j = 0 \quad (1.20)$$

Dividing through by $\hat{R}T$ and setting $\pi = -\lambda/\hat{R}T$ gives:

$$f_1 = \frac{\mu_j^\circ}{\hat{R}T} + \ln \frac{p}{p_{\text{ref}}} + \ln \mathcal{N}_j - \ln \mathcal{N} - \sum_{i=1}^{\text{NE}} \pi_i a_{i,j} - \pi_q q_j = 0 \quad (1.21)$$

We now need to take the partial derivatives of our functions wrt our non-linear variables as well as each π , and then multiple it by the correction variables.

You can easily take derviatives wrt $\ln x$ by converting from x to $\exp(\ln x)$.

$$\frac{\partial f_1}{\partial [\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \Delta \ln \mathcal{N}_j \quad (1.22)$$

$$\frac{\partial f_1}{\partial [\ln \mathcal{N}]} \Delta \ln \mathcal{N} = -\Delta \ln \mathcal{N} \quad (1.23)$$

$$\frac{\partial f_1}{\partial [\ln T]} \Delta \ln T = -\frac{H_j^\circ}{\hat{R}T} \Delta \ln T \quad (1.24)$$

$$\frac{\partial f_1}{\partial [\pi_i]} \pi_i = -a_{ij} \pi_i \quad (1.25)$$

$$\frac{\partial f_1}{\partial [\pi_q]} \pi_q = -q_j \pi_q \quad (1.26)$$

Combining these into the form of equation [1.4] gives

$$\Delta \ln \mathcal{N}_j - \Delta \ln \mathcal{N} - \sum_{i=1}^{\text{NE}} a_{ij} \pi_i - q_j \pi_q - \frac{H_j^\circ}{\hat{R}T} \Delta \ln T = \mu_j + \sum_{i=1}^{\text{NE}} \pi_i a_{ij} + \pi_q q_j \quad (1.27)$$

From before, the argument is made that $\pi_i = 0$ at the start of every iteration, so this equation becomes:

$$\Delta \ln \mathcal{N}_j - \Delta \ln \mathcal{N} - \sum_{i=1}^{\text{NE}} a_{ij} \pi_i - q_j \pi_q - \frac{H_j^\circ}{\hat{R}T} \Delta \ln T = -\frac{\mu_j}{\hat{R}T}$$

There will be one of these equation for each species.

1.4.4 Derivatives of f_2

$$\frac{\partial f_2}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = a_{ij} \mathcal{N}_j \Delta \ln \mathcal{N}_j \quad (1.28)$$

$$\frac{\partial f_2}{\partial[\ln \mathcal{N}]} \Delta \ln \mathcal{N} = \frac{\partial f_2}{\partial[\pi_i]} \pi_i = \frac{\partial f_2}{\partial[\ln T]} = \frac{\partial f_2}{\partial[\pi_q]} \pi_q = 0 \quad (1.29)$$

Which gives:

$$\boxed{\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \Delta \ln \mathcal{N}_j = b_i^\circ - \sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j}$$

1.4.5 Derivatives of f_3

$$\frac{\partial f_3}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = q_j \mathcal{N}_j \Delta \ln \mathcal{N}_j \quad (1.30)$$

$$\frac{\partial f_3}{\partial[\ln \mathcal{N}]} \Delta \ln \mathcal{N} = \frac{\partial f_3}{\partial[\ln T]} = \frac{\partial f_3}{\partial[\pi_i]} \pi_i = \frac{\partial f_3}{\partial[\pi_q]} \pi_q = 0 \quad (1.31)$$

Giving:

$$\boxed{\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \Delta \ln \mathcal{N}_j = - \sum_{j=1}^{\text{NS}} q_i \mathcal{N}_j}$$

1.4.6 Derivatives of f_4

$$\frac{\partial f_4}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \mathcal{N}_j \Delta \ln \mathcal{N}_j \quad (1.32)$$

$$\frac{\partial f_4}{\partial[\ln \mathcal{N}]} \Delta \ln \mathcal{N} = -\mathcal{N} \Delta \ln \mathcal{N} \quad (1.33)$$

$$\frac{\partial f_4}{\partial[\ln T]} = \frac{\partial f_4}{\partial[\pi_i]} \pi_i = \frac{\partial f_4}{\partial[\pi_q]} \pi_q = 0 \quad (1.34)$$

$$\boxed{\sum_{j=1}^{\text{NS}} \mathcal{N}_j \Delta \ln \mathcal{N}_j - \mathcal{N} \Delta \ln \mathcal{N} = \mathcal{N} - \sum_{j=1}^{\text{N}} \mathcal{N}_j} \quad (1.35)$$

1.4.7 Derivatives of f_5

$$\frac{\partial f_5}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \Delta \ln \mathcal{N}_j \quad (1.36)$$

$$\frac{\partial f_5}{\partial[\ln T]} = \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \Delta \ln T \quad (1.37)$$

$$\frac{\partial f_5}{\partial[\ln \mathcal{N}]} \Delta \ln \mathcal{N} = \frac{\partial f_5}{\partial[\pi_i]} \pi_i = \frac{\partial f_5}{\partial[\pi_q]} \pi_q = 0 \quad (1.38)$$

Giving:

$$\boxed{\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \Delta \ln \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \Delta \ln T = \frac{h' - h'_0}{\hat{R}T}}$$

1.4.8 Derivatives of f_6

$$\frac{\partial f_6}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \mathcal{N}_j \frac{S_j}{\hat{R}} \Delta \ln \mathcal{N}_j \quad (1.39)$$

$$\frac{\partial f_6}{\partial[\ln T]} = \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \Delta \ln T \quad (1.40)$$

$$\frac{\partial f_6}{\partial[\ln \mathcal{N}]} \Delta \ln \mathcal{N} = \frac{\partial f_6}{\partial[\pi_i]} \pi_i = \frac{\partial f_6}{\partial[\pi_q]} \pi_q = 0 \quad (1.41)$$

Giving

$$\boxed{\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{S_j}{\hat{R}} \Delta \ln \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \Delta \ln T = \frac{s'_0 - s'}{\hat{R}} + \mathcal{N} - \sum_{j=1}^{\text{NS}} \mathcal{N}_j}$$

All six of the equations are now listed for convenience:

$$\Delta \ln \mathcal{N}_j - \Delta \ln \mathcal{N} - \sum_{i=1}^{\text{NE}} a_{ij} \pi_i - q_j \pi_q - \frac{H_j^\circ}{\hat{R}T} \Delta \ln T = -\frac{\mu_j}{\hat{R}T} \quad (1.42)$$

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j \Delta \ln \mathcal{N}_j - \mathcal{N} \Delta \ln \mathcal{N} = \mathcal{N} - \sum_{j=1}^{\text{NS}} \mathcal{N}_j \quad (1.43)$$

$$\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \Delta \ln \mathcal{N}_j = b_i^\circ - \sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \quad (1.44)$$

$$\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \Delta \ln \mathcal{N}_j = - \sum_{j=1}^{\text{NS}} q_i \mathcal{N}_j \quad (1.45)$$

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \Delta \ln \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \Delta \ln T = \frac{h'_0 - h'}{\hat{R}T} \quad (1.46)$$

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{S_j}{\hat{R}} \Delta \ln \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \Delta \ln T = \frac{s'_0 - s'}{\hat{R}} + \mathcal{N} - \sum_{j=1}^{\text{NS}} \mathcal{N}_j \quad (1.47)$$

1.4.9 Reduced Gibbs Equations

A shortcut can be made to make this system of equations smaller. This is achieved by solving equation [1.42] for $\Delta \ln \mathcal{N}_j$ and plugging it into equations [1.43] - [1.47]

$$\Delta \ln \mathcal{N}_j = \Delta \ln \mathcal{N} + \sum_{i=1}^{\text{NE}} a_{ij} \pi_i - \frac{\mu_j}{\hat{R}T} + q_j \pi_q + \frac{H_j^\circ}{\hat{R}T} \Delta \ln T \quad (1.48)$$

Substitution into equation [1.44] - [1.47] yields:

$$\begin{aligned} \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{kj} a_{ij} \mathcal{N}_j \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j \right] \Delta \ln \mathcal{N} + \left[\sum_{j=1}^{\text{NS}} a_{kj} q_j \mathcal{N}_j \right] \pi_q + \left[\sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \right] \Delta \ln T \\ = b_k^\circ - \sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j + \sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j \frac{\mu_j}{\hat{R}T} \end{aligned} \quad (1.49)$$

$$\begin{aligned}
& \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j - \mathcal{N} \right] \Delta \ln \mathcal{N} + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \right] \pi_q + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \right] \Delta \ln T \\
& = \mathcal{N} - \sum_{j=1}^{\text{NS}} \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{\mu_j}{\hat{R}T} \quad (1.50)
\end{aligned}$$

$$\begin{aligned}
& \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} q_j \mathcal{N}_j \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \right] \Delta \ln \mathcal{N} + \left[\sum_{j=1}^{\text{NS}} q_j^2 \mathcal{N}_j \right] \pi_q + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \right] \Delta \ln T \\
& = \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{\mu_j}{\hat{R}T} - \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \quad (1.51)
\end{aligned}$$

$$\begin{aligned}
& \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \right] \Delta \ln \mathcal{N} + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \right] \pi_q \\
& + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \left(\frac{H_j^\circ}{\hat{R}T} \right)^2 + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \right] \Delta \ln T = \frac{h'_0 - h'}{\hat{R}T} + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{H_j^\circ}{\hat{R}T} \frac{\mu_j}{\hat{R}T} \quad (1.52)
\end{aligned}$$

$$\begin{aligned}
& \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \frac{S_j}{\hat{R}} \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{S_j}{\hat{R}} \right] \Delta \ln \mathcal{N} + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{S_j}{\hat{R}} \right] \pi_q \\
& + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{S_j}{\hat{R}} \frac{H_j^\circ}{\hat{R}T} + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{p,j}^\circ}{\hat{R}} \right] \Delta \ln T = \frac{s'_0 - s'}{\hat{R}} + \mathcal{N} - \sum_{j=1}^{\text{NS}} \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{S_j}{\hat{R}} \frac{\mu_j}{\hat{R}T} \quad (1.53)
\end{aligned}$$

There are NE number of equation [1.50], and only one of all others. Once this system has been solved, you recover \mathcal{N}_j with equation [1.48].

The equations are colored according to when they are needed. **Red coloring** denotes terms that arise from the elemental constraint condition. These are included no matter what. **Blue** denotes terms that are added when you include the charge constraint. **Violet** terms are added for both HP and SP constraints.

orange and teal are the rows added for enthalpy or entropy constraints, respectively.

1.5 Helmholtz Minimization

The Helmholtz energy is defined as:

$$F = G - pV \quad (1.54)$$

Where G is the Gibbs free energy, p is the pressure, and V is the volume. Substitution of G yields:

$$F = \sum_{j=1}^{\text{NS}} \mu_j \mathcal{N}_j - pV \quad (1.55)$$

Where the chemical potential is redefined as:

$$\mu_j = \mu_j^\circ + \hat{R}T \ln \left(\frac{\mathcal{N}_j R' T}{V} \right) \quad (1.56)$$

and $R' = \hat{R} \cdot 10^{-5}$ is the same as dividing \hat{R} by the reference pressure of 1 bar.

1.5.1 Constraints

The constraints available for the Helmholtz energy are:

- Hold temperature (T) and volume (V) constant.
- Hold internal energy (U) and volume (V) constant.
- Hold entropy (S) and volume (V) constant.

For (TV) minimization, only the elemental and charge (if present) constraints are necessary. For (UV) minimization, the constraint is defined by:

$$u' - u'_0 = 0 \quad (1.57)$$

Where u'_0 is the specified internal energy, and u' is solved for during the minimization process as:

$$u' = \sum_{j=1}^{\text{NS}} \mathcal{N}_j U_j^\circ = u'_0 \quad (1.58)$$

As stated before, special care needs to be taken to include the enthalpies of formation and reference enthalpies if applicable. For (SV) minimization, the constraint is defined by:

$$s' - s'_0 = 0 \quad (1.59)$$

Where s'_0 is the specified entropy and s' is solved for during the minimization process as:

$$s' = \sum_{j=1}^{\text{NS}} \mathcal{N}_j S_j \quad (1.60)$$

where:

$$S_j = S_j^\circ - \hat{R} \ln \mathcal{N}_j - \hat{R} \ln \left(\frac{R'T}{V} \right) \quad (1.61)$$

The Lagrangian for the Helmholtz energy minimization process is then defined as:

$$\mathcal{L} = \sum_{j=1}^{\text{NS}} \mu_j \mathcal{N}_j - pV + \sum_{i=1}^{\text{NE}} \lambda_i \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j - b_i^\circ \right] + \lambda_q \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \right] \quad (1.62)$$

1.5.2 Derivatives

We first find our functions f that are equal to 0 by taking the derivatives wrt \mathcal{N}_j , λ_i , and λ_q :

$$f_1 = \frac{\partial \mathcal{L}}{\partial \mathcal{N}_j} = \mu_j + \sum_{i=1}^{\text{NE}} \lambda_i a_{ij} + \lambda_q q_j = 0 \quad (1.63)$$

$$f_2 = \frac{\partial \mathcal{L}}{\partial \lambda_i} = \sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j - b_i^\circ = 0 \quad (1.64)$$

$$f_3 = \frac{\partial \mathcal{L}}{\partial \lambda_q} = \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j - 0 = 0 \quad (1.65)$$

We now form the second derivatives that define our Jacobian in the Newton step. We expand the chemical potential term using equation 1.56 and non-dimensionalize the equation by $\hat{R}T$. We also set $\pi = -\lambda/\hat{R}T$.

1.5.3 Derivatives for f_1

The derivatives for f_1 are then:

$$\frac{\partial f_1}{\partial [\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \Delta \ln \mathcal{N}_j \quad (1.66)$$

$$\frac{\partial f_1}{\partial [\ln T]} \Delta \ln T = -\frac{U_j^\circ}{\hat{R}T} \ln T \quad (1.67)$$

$$\frac{\partial f_1}{\partial \pi_i} \pi_i = -a_{ij} \pi_i \quad (1.68)$$

$$\frac{\partial f_1}{\partial \pi_q} \pi_q = -q_j \pi_q \quad (1.69)$$

The derivation for equation [1.67] is carried out in more depth in section [2.2]. Therefore, our final result is:

$$\Delta \ln \mathcal{N}_j - \sum_{i=1}^{\text{NE}} a_{ij} \pi_i - q_j \pi_q - \frac{U_j^\circ}{\hat{R}T} \Delta \ln T = -\frac{\mu_j}{\hat{R}T}$$

There will be NS number of these equations in our system.

1.5.4 Derivatives for f_2

Next, we take the derivatives of f_2 :

$$\frac{\partial f_2}{\partial [\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \mathcal{N}_j a_{i,j} \Delta \ln \mathcal{N}_j \quad (1.70)$$

$$\frac{\partial f_2}{\partial [\ln T]} \Delta \ln T = \frac{\partial f_2}{\partial \pi_i} \pi_i = \frac{\partial f_2}{\partial \pi_q} \pi_q = 0 \quad (1.71)$$

Which gives:

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j a_{ij} \Delta \ln \mathcal{N}_j = b_i^\circ - \sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j$$

There will be NE of these equations.

1.5.5 Derivatives for f_3

For f_3 we get:

$$\frac{\partial f_3}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \mathcal{N}_j q_j \Delta \ln \mathcal{N}_j \quad (1.72)$$

$$\frac{\partial f_3}{\partial[\ln T]} \Delta \ln T = \frac{\partial f_3}{\partial \pi_i} \pi_i = \frac{\partial f_3}{\partial \pi_q} \pi_q = 0 \quad (1.73)$$

Which gives only one equation:

$$\boxed{\sum_{j=1}^{\text{NS}} \mathcal{N}_j q_j \Delta \ln \mathcal{N}_j = - \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j}$$

1.5.6 Derivatives for f_4

For internal energy, we have:

$$f_4(\ln \mathcal{N}_j, \ln T) = \sum_{j=1}^{\text{NS}} \mathcal{N}_j U_j^\circ - u'_0 = u' - u'_0 \quad (1.74)$$

Using identity [2.1] helps with the temperature derivative. The derivatives are then:

$$\frac{\partial f_4}{\partial[\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \frac{\mathcal{N}_j U_j^\circ}{\hat{R}T} \Delta \ln \mathcal{N}_j \quad (1.75)$$

$$\frac{\partial f_4}{\partial[\ln T]} \Delta \ln T = \sum_{j=1}^{\text{NS}} [T \mathcal{N}_j c_{v,j}^\circ] \Delta \ln T \quad (1.76)$$

$$\frac{\partial f_4}{\partial \pi_i} \pi_i = \frac{\partial f_4}{\partial \pi_q} \pi_q = 0 \quad (1.77)$$

After non-dimensionalizing, we are left with:

$$\boxed{\sum_{j=1}^{\text{NS}} \frac{\mathcal{N}_j U_j^\circ}{\hat{R}T} \Delta \ln \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \frac{\mathcal{N}_j c_{v,j}^\circ}{R} \Delta \ln T = \frac{u'_0 - u'}{\hat{R}T}}$$

1.5.7 Derivatives for f_5

For the entropy constraint we have:

$$f_5(\ln \mathcal{N}_j, \ln T) = \sum_{j=1}^{\text{NS}} \mathcal{N}_j S_j - s'_0 = s' - s'_0 \quad (1.78)$$

Again, identity [2.1] assists us. The derivates are:

$$\frac{\partial f_5}{\partial [\ln \mathcal{N}_j]} \Delta \ln \mathcal{N}_j = \mathcal{N}_j [S_j - \hat{R}] \Delta \ln \mathcal{N}_j \quad (1.79)$$

$$\frac{\partial f_5}{\partial [\ln T]} \Delta \ln T = \mathcal{N}_j c_{v,j}^\circ \Delta \ln T \quad (1.80)$$

$$\frac{\partial f_5}{\partial \pi_i} \pi_i = \frac{\partial f_5}{\partial \pi_q} \pi_q = 0 \quad (1.81)$$

Which, after non-dimensionalizing gives the singular equation:

$$\boxed{\sum_{j=1}^{\text{NS}} \mathcal{N}_j \left[\frac{S_j}{\hat{R}} - 1 \right] \Delta \ln \mathcal{N}_j + \mathcal{N}_j \frac{c_{v,j}^\circ}{\hat{R}} \Delta \ln T = \frac{s'_0 - s'}{\hat{R}}} \quad (1.82)$$

For convenience, they are all listed here together:

$$\Delta \ln \mathcal{N}_j - \sum_{i=1}^{\text{NE}} a_{ij} \pi_i - q_j \pi_q - \frac{U_j^\circ}{\hat{R}T} \Delta \ln T = -\frac{\mu_j}{\hat{R}T} \quad (1.83)$$

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j a_{ij} \Delta \ln \mathcal{N}_j = b_i^\circ - \sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \quad (1.84)$$

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j q_j \Delta \ln \mathcal{N}_j = - \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \quad (1.85)$$

$$\sum_{j=1}^{\text{NS}} \frac{\mathcal{N}_j U_j^\circ}{\hat{R}T} \Delta \ln \mathcal{N}_j + \sum_{j=1}^{\text{NS}} \frac{\mathcal{N}_j c_{v,j}^\circ}{R} \Delta \ln T = \frac{u'_0 - u'}{\hat{R}T} \quad (1.86)$$

$$\sum_{j=1}^{\text{NS}} \mathcal{N}_j \left[\frac{S_j}{\hat{R}} - 1 \right] \Delta \ln \mathcal{N}_j + \mathcal{N}_j \frac{c_{v,j}^\circ}{\hat{R}} \Delta \ln T = \frac{s'_0 - s'}{\hat{R}} \quad (1.87)$$

1.5.8 Reduced Helmholtz Equations

A "simplification" can be made to the above system of equations by solving equations [1.83] for $\Delta \ln \mathcal{N}_j$:

$$\Delta \ln \mathcal{N}_j = \sum_{i=1}^{\text{NE}} a_{i,j} \pi_i - \frac{\mu_j}{\hat{R}T} + q_j \pi_q + \frac{U_j^\circ}{\hat{R}T} \Delta \ln T \quad (1.88)$$

By substituting this into equations [1.84] - [1.87], we can shrink the system of equations dramatically. The resulting set of equations is:

$$\sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{kj} a_{ij} \mathcal{N}_j \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} a_{kj} q_j \mathcal{N}_j \right] \pi_q + \left[\sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j \frac{U_j^\circ}{\hat{R}T} \right] \Delta \ln T = b_k^\circ - \sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j + \sum_{j=1}^{\text{NS}} a_{kj} \mathcal{N}_j \frac{\mu_j}{\hat{R}T} \quad (1.89)$$

$$\sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} q_j \mathcal{N}_j \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} q_j^2 \mathcal{N}_j \right] \pi_q + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{U_j^\circ}{\hat{R}T} \right] \Delta \ln T = \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{\mu_j}{\hat{R}T} - \sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \quad (1.90)$$

$$\begin{aligned} \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \frac{U_j^\circ}{\hat{R}T} \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \frac{U_j^\circ}{\hat{R}T} \right] \pi_q + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \left(\frac{U_j^\circ}{\hat{R}T} \right)^2 + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{v,j}^\circ}{\hat{R}} \right] \Delta \ln T \\ = \frac{u'_0 - u'}{\hat{R}T} + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{U_j^\circ}{\hat{R}T} \frac{\mu_j}{\hat{R}T} \end{aligned} \quad (1.91)$$

$$\begin{aligned} \sum_{i=1}^{\text{NE}} \left[\sum_{j=1}^{\text{NS}} a_{ij} \mathcal{N}_j \left(\frac{S_j}{\hat{R}} - 1 \right) \right] \pi_i + \left[\sum_{j=1}^{\text{NS}} q_j \mathcal{N}_j \left(\frac{S_j}{\hat{R}} - 1 \right) \right] \pi_q \\ + \left[\sum_{j=1}^{\text{NS}} \mathcal{N}_j \left(\frac{S_j}{\hat{R}} - 1 \right) \frac{U_j^\circ}{\hat{R}T} + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{c_{v,j}^\circ}{\hat{R}} \right] \Delta \ln T = \frac{s'_0 - s'}{\hat{R}} + \sum_{j=1}^{\text{NS}} \mathcal{N}_j \frac{\mu_j}{\hat{R}T} \left(\frac{S_j}{\hat{R}} - 1 \right) \end{aligned} \quad (1.92)$$

There will be NE number of equations 1.89, and one of 1.90 if charge is added, and one of 1.91/1.92 depending on which one you made need.

The equations are colored according to when they are needed. **Red coloring** denotes terms that arise from the elemental constraint condition. These are included no matter what. **Blue** denotes terms that are added when you include

the charge constraint. **Violet** terms are added for both UV and SV constraints. **orange** and **teal** are the rows added for either internal energy or entropy constraints, respectively.

1.6 Useful Relationships

$$\frac{c_v^\circ}{\hat{R}} = \frac{c_{p,j}^\circ}{\hat{R}} - 1 \quad (1.93)$$

$$\frac{\mu_j^\circ}{\hat{R}T} = \frac{H_j^\circ}{\hat{R}T} - \frac{S_j^\circ}{\hat{R}} \quad (1.94)$$

$$\frac{U_j^\circ}{\hat{R}T} = \frac{H_j^\circ}{\hat{R}T} - 1 \quad (1.95)$$

2 Standard State Chemical Potential Derivatives

Some important derivatives are derived here. First, we state a chain rule identity that is very useful:

$$\frac{\partial}{\partial T} = \frac{\partial[\ln(T)]}{\partial T} \frac{\partial}{\partial[\ln(T)]} \rightarrow \frac{\partial}{\partial[\ln(T)]} = T \frac{\partial}{\partial T} \quad (2.1)$$

Then, taking the derivative of μ_j^0 gives:

$$\frac{\partial}{\partial[\ln(T)]} \left(\frac{\mu_j^0}{RT} \right) = T \frac{\partial}{\partial T} \left(\frac{\mu_j^0}{RT} \right) \quad (2.2)$$

We expand μ_j^0/RT as one of the following two equation depending on if we are using Gibbs or Helmholtz minimization:

$$\frac{\mu_j^0}{RT} = \frac{H_j^0}{RT} - \frac{S_j^0}{R} \quad (2.3)$$

$$\frac{\mu_j^0}{RT} = \frac{U_j^0}{RT} - \frac{S_j^0}{R} + 1 \quad (2.4)$$

2.1 Gibbs Derivative

First, we take the derivative of [2.3] for Gibbs minimization.

$$T \frac{\partial}{\partial T} \left(\frac{H_j^0}{RT} - \frac{S_j^0}{R} \right) = T \left(\frac{\partial_T(H_j^0) \cdot RT - H_j^0 \cdot R}{(RT)^2} - \frac{\partial_T(S_j^0)}{R} \right) \quad (2.5)$$

Here, ∂_T denotes $(\partial/\partial T)$. If:

$$c_{p,j}^0 = \frac{\partial H_j^0}{\partial T}, \text{ and } \frac{c_{p,j}^0}{T} = \frac{\partial S_j^0}{\partial T} \quad (2.6)$$

This reduces to:

$$T \left[\frac{c_{p,j}^0}{RT} - \frac{H_j^0}{RT^2} - \frac{c_{p,j}^0}{RT} \right] = -\frac{H_j^0}{RT} \quad (2.7)$$

Therefore:

$$\boxed{\frac{\partial}{\partial [\ln(T)]} \left(\frac{\mu_j^0}{RT} \right) = -\frac{H_j^0}{RT}} \quad (2.8)$$

2.2 Helmholtz Derivative

Using equation [2.4] gives us:

$$T \frac{\partial}{\partial T} \left(\frac{U_j^0}{RT} + 1 - \frac{S_j^0}{R} \right) = T \left(\frac{\partial_T(U_j^0) \cdot RT - U_j^0 \cdot R}{(RT)^2} - \frac{\partial_T(S_j^0)}{R} \right) \quad (2.9)$$

Recalling $\partial_T(S_j^0)$ from equation [2.6] and using:

$$c_{v,j}^0 = \frac{\partial U_j^0}{\partial T} \quad (2.10)$$

Equation [2.9] reduced to:

$$T \left[\frac{c_{v,j}^0}{RT} - \frac{U_j^0}{RT^2} - \frac{c_{p,j}^0}{RT} \right] \quad (2.11)$$

Since:

$$\frac{c_{v,j}^0}{R} - \frac{c_{p,j}^0}{R} = -1 \quad (2.12)$$

The final derivative is:

$$\frac{\partial}{\partial[\ln(T)]} \left(\frac{\mu_j^0}{RT} \right) = -\frac{U_j^0}{RT} - 1 \quad (2.13)$$

3 Code description

Currently, the University of Minnesota’s code is focused on Gibbs minimization holding TP constant, and Helmholtz minimization holding TV, and UV constant. Further development will include the other three auxiliary constraints. It also includes the charge constraint if ions are present in the mixture. The code comes with easily accessible function for common air mixtures such as 5, 7, and 11 species air for easy access to common mixtures of interest in aerospace applications. The ability to create mixtures from any user-specified mixture is available if necessary.

Access to all thermodynamic data is readily available through use of the object `mix`. By defining an object named ‘gas’ of type `mix`, the user can find all thermodynamic variables necessary after minimization by appending the correct suffix to ‘gas’, e.g., `gas.rho` contains mixture density, `gas.R` contains mixture gas constant, `gas.Y[j]` shows mass fraction of species j , etc. A function named `print_properties(gas)` will output all thermodynamic variables of the gas mixture to the terminal.

In the bin directory of this code, there are three programs ready to be run and/or edited after you build. The first is an example program (named `example.cpp`) that has everything defined for you to run it and see the minimization results. You can toy with options to understand how to use correct ‘enum class’ such as `ConstraintType::` (both defined below) and access results.

The second program is the command-line driven code that lets you choose options and set mixtures for the chemical equilibrium process. The program has a “help” command that will tell you what you need to run. An overview is given here as well. When you start the program, it will give you some options right off the bat. In order to run minimization, all fields need to filled in that appear when you type “show”. The “-constraint” field initialized by default to use the TP constraint, though it can readily be changed.

The ‘-mode’ option tells the program which mode it is running in. By inputting ‘-mode= sweep’ you can change the program from a standalone minimization given a single values for minimization parameters, to a version that sweeps through an user-input min and max energy value and then plots the results to a user-named file.

The ‘-constraint’ option tells the programs with minimization procedure to use. TP, TV, UV, CFD are the current ones available. It needs to be in caps when input as well. For example ‘-constraint=TP’.

The ‘-species’ option tells the program which species you want to include in the minimization process. You can list your own with comma separated variables as such: ‘-species= N2, O2, NO, N, O’. If you choose to build a species list this way, you will need to specify a couple more things like ‘-elements’ and ‘-Y’. If instead you use an already created mixture (available ones are air5, air7, air11, air13, mars8), you can do so with ‘-species= air11’. This will fill in the ‘-elements’ and ‘-Y’ flags for you as well. You can always double check what needs to be filled in with the ‘show’ command.

If you do need to specify elements and mass fractions, you can do so with ‘-elements= N, O’ and also ‘-Y= 0.7572, 0.2428’. Just make sure that the order that you input the mass fractions lines up with the elemental ordering.

When the configuration input has been filled in, typing ”run” in the command line will run the program for you. You will still need to follow command line prompts for specifying filenames, sweeping values, etc.

Finally, the third program is created for timing the speed of the minimization processes and is really more for developing than for getting values.