

# Contents

<b>9</b>	<b>Reacting mixtures of ideal gases</b>	<b>9-1</b>
9.1	Introduction . . . . .	9-1
9.2	Ideal mixtures . . . . .	9-3
9.3	Criterion for equilibrium . . . . .	9-5
9.4	The entropy of mixing . . . . .	9-6
9.5	Enthalpy . . . . .	9-10
9.5.1	Enthalpy of formation and the reference reaction . . . . .	9-11
9.6	Chemical equilibrium, the method of element potentials . . . . .	9-13
9.7	Example - combustion of carbon monoxide . . . . .	9-18
9.7.1	Adiabatic flame temperature . . . . .	9-22
9.7.2	Isentropic expansion . . . . .	9-24
9.7.3	Nozzle expansion . . . . .	9-25
9.8	Rocket performance using CEA . . . . .	9-26

# Chapter 9

## Reacting mixtures of ideal gases

### 9.1 Introduction

This is a condensed version of Chapter 9 of the AA283 course reader. The discussion of the element potential method for chemical equilibrium is limited to gas phase reactions only.

For an open system containing several reacting chemical species that can exchange mass and work with its surroundings the fundamental Gibbs equation relating equilibrium states is

$$TdS = dE + PdV - \sum_{i=1}^I \mu_i dn_i + \sum_{k=1}^K F_k dl_k. \quad (9.1)$$

The  $F_k$  are forces that can act on the system through differential displacements. Ordinarily, lower case letters will be used to denote intensive (per unit mole) quantities ( $h, s, e, etc$ ) and upper case will designate extensive quantities ( $H, S, E, etc$ ). Heat capacities, pressure and temperature are symbolized in capital letters. One mole is an Avagadro's number of molecules,  $6.0221415 \times 10^{23}$ .

The chemical potential energy per unit mole  $\mu_i$  is the amount by which the extensive energy of the system is changed when a differential number of moles  $dn_i$  of species  $i$  is added or removed from the system. If the system is closed so no mass can enter or leave and if it is

isolated from external forces, the Gibbs equation becomes

$$TdS = dE + PdV - \sum_{i=1}^I \mu_i dn_i \quad (9.2)$$

where the differential changes in the number of moles of species  $i$  occur through chemical reactions that may take place within the closed volume. The main difference between (9.1) and (9.2) is that, in the closed system, changes in mole numbers are subject to the constraint that the number of atoms of each element in the system is strictly constant. The precise expression of the chemical potential in terms of conventional thermodynamic variables of state will be established shortly. For the present it can be regarded as a new, intensive state variable for the species  $i$ . Mathematically, equation (9.2) implies that

$$\mu_i(E, V, n_1, \dots, n_I) = -T \left( \frac{\partial S}{\partial n_i} \right)_{E, V, n_{j \neq i}}. \quad (9.3)$$

If no reactions occur then (9.2) reduces to the familiar form

$$TdS = dE + PdV. \quad (9.4)$$

According to the second law of thermodynamics, for *any* process of a closed, isolated system

$$TdS \geq dE + PdV. \quad (9.5)$$

Spatial gradients in any variable of the system can lead to an increase in the entropy. Smoothing out of velocity gradients (kinetic energy dissipation) and temperature gradients (temperature dissipation) constitute the two most important physical mechanisms that contribute to the increase in entropy experienced by a non-reacting system during a non-equilibrium process. If the system contains a set of chemical species that can mix, then changes in entropy can also occur through the smoothing out of concentration gradients for the various species. If the species can react, then entropy changes will occur through changes in the chemical binding energy of the various species undergoing reactions.

The inequality (9.5) can be used to establish the direction of a thermodynamic system as it evolves toward a state of equilibrium.

## 9.2 Ideal mixtures

Consider a mixture of species with mole numbers  $(n_1, n_2, \dots, n_I)$ . The extensive internal energy of the system is  $E$  and the volume is  $V$ . The extensive entropy of the system is the function,  $S(E, V, n_1, n_2, \dots, n_I)$ . An ideal mixture is one where all molecules experience the same intermolecular forces. In an ideal mixture surface effects, (surface energy and surface tension) can be neglected and the enthalpy change when the constituents are mixed is zero. Ideal mixtures obey Raoult's law that states that the vapor pressure of a component of an ideal mixture is equal to the vapor pressure of the pure component times the mole fraction of that component in the mixture. In the ideal approximation the volume of the system is the sum of the volumes occupied by the pure species alone. Similarly the internal energy is the sum of internal energies of the pure species. Most real mixtures approximate ideal behavior to one degree or another. A mixture of ideal gases is perhaps the best example of an ideal mixture. Liquid mixtures where the component molecules are chemically similar, such as a mixture of benzene and toluene, behave nearly ideally. Mixtures of strongly different molecules such as water and alcohol deviate considerably from ideal behavior.

Let the mole numbers of the mixture be scaled by a common factor  $\alpha$ .

$$n_1 = \alpha \tilde{n}_1, \quad n_2 = \alpha \tilde{n}_2, \quad n_3 = \alpha \tilde{n}_3, \dots, \quad n_I = \alpha \tilde{n}_I \quad (9.6)$$

According to the ideal assumption, the extensive properties of the system will scale by the same factor.

$$E = \alpha \tilde{E}, \quad V = \alpha \tilde{V} \quad (9.7)$$

Similarly the extensive entropy of the system scales as

$$S(E, V, n_1, \dots, n_I) = \alpha \tilde{S}(\tilde{E}, \tilde{V}, \tilde{n}_1, \dots, \tilde{n}_I). \quad (9.8)$$

Functions that follow this scaling are said to be homogeneous functions of order one. Differentiate (9.8) with respect to  $\alpha$ .

$$\tilde{E} \frac{\partial S}{\partial E} + \tilde{V} \frac{\partial S}{\partial V} + \sum_{i=1}^I \tilde{n}_i \frac{\partial S}{\partial n_i} = \tilde{S}(\tilde{E}, \tilde{V}, \tilde{n}_1, \dots, \tilde{n}_I) \quad (9.9)$$

Multiply (9.9) by  $\alpha$  and substitute (9.8).

$$E \frac{\partial S}{\partial E} + V \frac{\partial S}{\partial V} + \sum_{i=1}^I n_i \frac{\partial S}{\partial n_i} = S(E, V, n_1, \dots, n_I) \quad (9.10)$$

The Gibbs equation is

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \sum_{i=1}^I \frac{\mu_i}{T} dn_i. \quad (9.11)$$

According to (9.11) the partial derivatives of the entropy are

$$\begin{aligned} \frac{\partial S}{\partial E} &= \frac{1}{T} \\ \frac{\partial S}{\partial V} &= \frac{P}{T} \\ \frac{\partial S}{\partial n_i} &= -\frac{\mu_i}{T}. \end{aligned} \quad (9.12)$$

Inserting (9.12) into (9.10) leads to a remarkable result for an ideal mixture.

$$E + PV - TS = \sum_{i=1}^I n_i \mu_i \quad (9.13)$$

Equation (9.13) is called the Duhem-Gibbs relation. The combination of state variables that appears in (9.13) is called the Gibbs free energy.

$$G = E + PV - TS = H - TS \quad (9.14)$$

Equation (9.13) expresses the extensive Gibbs free energy of an ideal mixture in terms of the mole numbers and chemical potentials.

$$G = \sum_{i=1}^I n_i \mu_i \quad (9.15)$$

This important result shows that the chemical potential of species  $i$  is not really a new state variable but is defined in terms of the familiar state variables, enthalpy, temperature and entropy. The chemical potential of species  $i$  is its *molar* Gibbs free energy.

$$\mu_i = g_i = h_i - Ts_i \quad (9.16)$$

The enthalpy in (9.16) includes the chemical enthalpy associated with the formation of the species from its constituent elements.

### 9.3 Criterion for equilibrium

The Gibbs free energy is sometimes described as the "escaping tendency" of a substance. At low temperatures the enthalpy dominates. A chemical species with a positive enthalpy would like to break apart releasing some of its chemical enthalpy as heat and producing products with lower enthalpy. A few examples are ozone ( $O_3$ ), hydrogen peroxide ( $H_2O_2$ ), and nitrous oxide ( $N_2O$ ). These are stable chemicals at room temperature but will decompose readily if their activation energy is exceeded in the presence of a heat source or a catalyst. The entropy of any substance is positive and at high temperatures the entropy term dominates the Gibbs free energy. In a chemical reaction the Gibbs free energy of any species or mixture will increasingly tend toward a state of higher entropy and lower Gibbs free energy as the temperature is increased. Take the differential of the Gibbs free energy.

$$dG = dE + PdV + VdP - TdS - SdT \quad (9.17)$$

For a process that takes place at constant temperature and pressure  $dT = dP = 0$ . The Second Law (9.5) leads to the result that for such a process

$$dG = dE + PdV - TdS \leq 0. \quad (9.18)$$

A spontaneous change of a system at constant temperature and pressure leads to a decrease of the Gibbs free energy. Equilibrium of the system is established when the Gibbs free energy reaches a minimum. This result leads to a complete theory for the equilibrium of a reacting system.

## 9.4 The entropy of mixing

Consider the adiabatic system shown in Figure 9.1 consisting of a set of  $(n_1, n_2, \dots, n_i, \dots, n_I)$  moles of gas species segregated into volumes of various sizes such that the volumes are all at the same temperature and pressure.

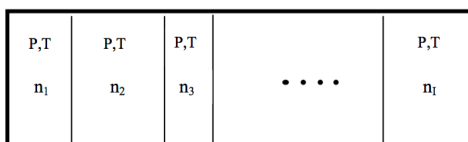


Figure 9.1: A system of gases separated by partitions.

The total number of moles in the system is

$$N = \sum_{i=1}^I n_i. \quad (9.19)$$

The entropy per unit mole of an ideal gas is determined using the Gibbs equation

$$ds = C_p \frac{dT}{T} - R_u \frac{dP}{P} \quad (9.20)$$

where the units of  $C_p$  are *Joules/(mole-Kelvin)*. Tabulations of gas properties are always defined with respect to a reference temperature and standard pressure. The reference temperature is universally agreed to be  $T_{ref} = 298.15 \text{ K}$  and the standard pressure is

$$P^\circ = 10^5 \text{ N/m}^2 = 10^5 \text{ Pascals} = 10^2 \text{ kPa} = 1 \text{ bar}. \quad (9.21)$$

All pressures are referred to  $P^\circ$  and the superscript '°' denotes a species property evaluated at standard pressure. A cautionary note: In 1999 the International Union of Pure and Applied Chemistry (IUPAC) recommended that for evaluating the properties of all substances, the standard pressure should be taken to be precisely  $100 \text{ kPa}$ . Prior to this date, the standard pressure was taken to be one atmosphere at sea level, which is  $101.325 \text{ kPa}$ . Tabulations prior to 1999 are standardized to this value. The main effect is a small change in the standard entropy of a substance at a given temperature tabulated before and after 1999. There are also small differences in heat capacity and enthalpy as well. The IUPAC continues to provide standards for chemistry calculations and chemical nomenclature.

The pressure has no effect on the heat capacity of ideal gases, and for many condensed species the effect of pressure on heat capacity is relatively small. For this reason, tabulations of thermodynamic properties at standard pressure can be used to analyze a wide variety of chemical phenomena involving condensed and gas phase mixtures. Inaccuracies occur when evaluations of thermodynamic properties involve phase changes or critical phenomena where wide deviations from the ideal gas law occur, or condensed phases exhibit significant compressibility.

Integrating (9.20) from the reference temperature at standard pressure, the entropy per unit mole of the *i*th gas species is

$$s_i(T, P) - s_i^\circ(T_{ref}) = \int_{T_{ref}}^T C_{pi}^\circ(T) \frac{dT}{T} - R_u \ln \left( \frac{P}{P^\circ} \right). \quad (9.22)$$

where the molar heat capacity  $C_{pi}^\circ$  is tabulated as a function of temperature at standard pressure. The standard entropy of a gas species at the reference temperature is

$$s_i^\circ(T_{ref}) = \int_0^{T_{ref}} C_{pi}^\circ(T) \frac{dT}{T} + s_i^\circ(0) \quad (9.23)$$

where the integration is carried out at  $P = P^\circ$ . To evaluate the standard entropy, heat capacity data is required down to absolute zero. For virtually all substances, with the exception of superfluid helium (II), the heat capacity falls off rapidly as  $T \rightarrow 0$  so that the integral in (9.23) converges despite the apparent singularity at  $T = 0$ . From the third law, the entropy constant at absolute zero,  $s_i^\circ(0)$ , is generally taken to be zero for a pure substance in its simplest crystalline state. For alloys and pure substances such as CO where more than one crystalline structure is possible, the entropy at absolute zero may be nonzero and tabulated entropy data for a substance may be revised from time to time as new research results become available. Generally the entropy constant is very small.

The entropy per unit mole of the *i*th gas species is

$$s_i(T, P) = s_i^\circ(T) - R_u \ln \left( \frac{P}{P^\circ} \right). \quad (9.24)$$

The entire effect of pressure on the system is in the logarithmic term of the entropy. The extensive entropy of the whole system before mixing is

$$S_{before} = \sum_{i=1}^I n_i s_i(T, P) = \sum_{i=1}^I n_i s_i^\circ(T) - \sum_{i=1}^I n_i R_u \ln \left( \frac{P}{P^\circ} \right). \quad (9.25)$$



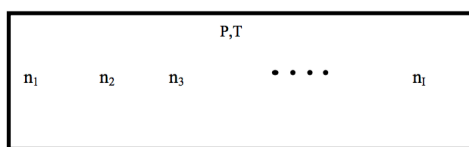


Figure 9.2: System of gases with the partitions removed at the same pressure, temperature and total volume as in Figure 9.1.

If the partitions are removed as shown in Figure 9.2 then, after complete mixing, each gas takes up the entire volume and the entropy of the  $i$ th species is

$$s_i(T, P_i) = s_i^\circ(T) - R_u \ln \left( \frac{P_i}{P^\circ} \right). \quad (9.26)$$

where  $P_i$  is the partial pressure of the  $i$ th species. The mixture is ideal so there is no enthalpy change during the mixing. If the pressure was so high that the potential energy associated with inter-molecular forces was significant then the enthalpy of mixing would be non-zero.

The entropy of the system after mixing is

$$S_{after} = \sum_{i=1}^I n_i s_i(T, P) = \sum_{i=1}^I n_i s_i^\circ(T) - \sum_{i=1}^I n_i R_u \ln \left( \frac{P_i}{P^\circ} \right). \quad (9.27)$$

The change of entropy due to mixing is

$$S_{after} - S_{before} = \left( \sum_{i=1}^I n_i s_i^\circ(T) - \sum_{i=1}^I n_i R_u \ln \left( \frac{P_i}{P^\circ} \right) \right) - \left( \sum_{i=1}^I n_i s_i^\circ(T) - \sum_{i=1}^I n_i R_u \ln \left( \frac{P}{P^\circ} \right) \right). \quad (9.28)$$

Cancel common terms in (9.28).

$$S_{after} - S_{before} = R_u \sum_{i=1}^I n_i \ln \left( \frac{P}{P_i} \right) > 0 \quad (9.29)$$

Mixing clearly leads to an increase in entropy. To determine the law that governs the partial pressure let's use the method of Lagrange multipliers to seek a maximum in the

entropy after mixing subject to the constraint that

$$P = \sum_{i=1}^I P_i. \quad (9.30)$$

That is, we seek a maximum in the function

$$W(T, n_1, n_2, \dots, n_I, P_1, P_2, \dots, P_I, \lambda) = \sum_{i=1}^I n_i s_i^\circ(T) - \sum_{i=1}^I n_i R_u \ln \left( \frac{P_i}{P^\circ} \right) + \lambda \left( \sum_{i=1}^I P_i - P \right) \quad (9.31)$$

where  $\lambda$  is an, as yet unknown, Lagrange multiplier. The temperature of the system and number of moles of each species in the mixture are constant. Differentiate (9.31) and set the differential to zero for an extremum.

$$dW = \frac{\partial W}{\partial P_1} dP_1 + \frac{\partial W}{\partial P_2} dP_2 + \dots + \frac{\partial W}{\partial P_I} dP_I + \frac{\partial W}{\partial \lambda} d\lambda = 0 \quad (9.32)$$

Now

$$dW = - \sum_{i=1}^I n_i R_u \left( \frac{dP_i}{P_i} \right) + \lambda \left( \sum_{i=1}^I dP_i \right) + d\lambda \left( \sum_{i=1}^I P_i - P \right) = 0. \quad (9.33)$$

The last term in (9.33) is zero by the constraint and the maximum entropy condition becomes.

$$\sum_{i=1}^I \left( -\frac{n_i R_u}{P_i} + \lambda \right) dP_i = 0 \quad (9.34)$$

Since the  $dP_i$  are completely independent, the only way (9.34) can be satisfied is if the Lagrange multiplier satisfies

$$\lambda = \frac{n_i R_u}{P_i} \quad (9.35)$$

for all  $i$ . In the original, unmixed, system each species satisfies the ideal gas law.

$$PV_i = n_i R_u T \quad (9.36)$$

Using (9.35) and (9.36) we can form the sum

$$\lambda \sum_{i=1}^I P_i = \sum_{i=1}^I \frac{PV_i}{T} . \quad (9.37)$$

Finally the Lagrange multiplier is

$$\lambda = \frac{V}{T} \quad (9.38)$$

where,  $V = \sum_{i=1}^I V_i$ . Using (9.35) and (9.38) the partial pressure satisfies

$$P_i V = n_i R_u T \quad (9.39)$$

which is Dalton's law of partial pressures. What we learn from this exercise is, not only that the entropy increases when the gases mix, but that the equilibrium state is one where the entropy is a maximum. Using Dalton's law, the mole fraction of the  $i$ th gas species is related to the partial pressure as follows

$$x_i = \frac{n_i}{N} = \frac{P_i}{P} \quad (9.40)$$

The entropy of a mixture of ideal gases expressed in terms of mole fractions is

$$S_{gas} = \sum_{i=1}^I n_i (s_{i_{gas}}^{\circ}(T) - R_u \ln(x_i)) - N R_u \ln\left(\frac{P}{P^{\circ}}\right) \quad (9.41)$$

and the entropy change due to mixing, (9.29), is expressed as

$$S_{after} - S_{before} = -N R_u \sum_{i=1}^I x_i \ln(x_i) > 0. \quad (9.42)$$

## 9.5 Enthalpy

The enthalpy per unit mole of a gas is determined from

$$dh = C_p(T) dT. \quad (9.43)$$

The enthalpy of a gas species is

$$h_i(T) - h_i(T_{ref}) = h_i^\circ(T) - h_i^\circ(T_{ref}) = \int_{T_{ref}}^T C_{pi}^\circ(T) dT. \quad (9.44)$$

In principle the standard enthalpy of the  $i$ th gas species at the reference temperature could be taken as

$$h_i^\circ(T_{ref}) = \int_0^{T_{ref}} C_{pi}^\circ dT + h_i^\circ(0). \quad (9.45)$$

In this approach the enthalpy constant is the enthalpy change associated with chemical bond breaking and making that occurs when the atoms composing the species are brought together from infinity to form the molecule at absolute zero. Note that even for an atomic species, the enthalpy constant is not exactly zero. A quantum mechanical system contains energy or enthalpy arising from ground state motions that cannot be removed completely even at absolute zero temperature. In practice, enthalpies for most substances are tabulated as differences from the enthalpy at the reference temperature of 298.15K which is much more easily accessible than absolute zero so the question of the zero point enthalpy rarely comes up. Thus the standard enthalpy of a species is

$$h_i^\circ(T) = \int_{T_{ref}}^T C_{pi}^\circ(T) dT + \Delta h_{fi}^\circ(T_{ref}) \quad (9.46)$$

where  $\Delta h_{fi}^\circ(T)$  is the enthalpy change that occurs when the atoms of the species are brought together from at infinity at the finite temperature  $T$ . The enthalpy including the heat of formation (9.46) is sometimes called the complete enthalpy. In practice certain conventions are used to facilitate the tabulation of the heat of formation of a substance.

### 9.5.1 Enthalpy of formation and the reference reaction

The enthalpy of formation of a substance, denoted  $\Delta h_f^\circ(T_{ref})$ , is defined as the enthalpy change that occurs when one mole of the substance is formed from its elements in their reference state at the given temperature  $T$  and standard pressure  $P^\circ$ . The reference state for an element is generally taken to be its most stable state at the given temperature and standard pressure. The reference reaction for a substance is one where the substance is the single product of a chemical reaction between its elements in their most stable state.

This convention for defining the heat of formation of a substance is useful even if the reference reaction is physically unlikely to ever actually occur. A consequence of this

definition is that the heat of formation of a pure element in its reference state at any temperature is always zero. For example, the enthalpy of formation of any of the diatomic gases is zero at all temperatures. This is clear when we write the trivial reaction to form, for example hydrogen, from its elements in their reference state.

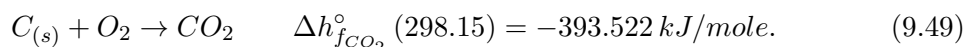


The enthalpy change is clearly zero. In fact the change in any thermodynamic variable for any element in its reference state is zero at all temperatures. A similar reference reaction applies to any of the other diatomic species  $O_2$ ,  $N_2$ ,  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ , and the heat of formation of these substances is zero at all temperatures. The most stable form of carbon is solid carbon or graphite and the reference reaction is



with zero heat of formation at all temperatures.

The reference reaction for carbon dioxide at  $298.15K$  is



Here the carbon is taken to be in the solid (graphite) form and the oxygen is taken to be the diatomic form. Both are the most stable forms over a wide range of temperatures. Even if the temperature is well above the point where carbon sublimates to a gas ( $3915 K$ ) and significant oxygen is dissociated, the heats of formation of  $C_{(s)}$  and  $O_2$  remain zero even though the most stable form of carbon at this temperature is carbon gas.

The heats of formation of metal elements are treated a little differently. The heat of formation of crystalline aluminum is zero at temperatures below the melting point and the heat of formation of liquid aluminum is zero at temperatures above the melting point. The same applies to boron, magnesium, sulfur, titanium and other metals.

The enthalpy (9.46) is usually expressed in terms of tabulated data as

$$h_i(T) = h_i^\circ(T) = \Delta h_{fi}^\circ(T_{ref}) + \{h_i^\circ(T) - h_i^\circ(T_{ref})\}. \quad (9.50)$$

For a general reaction the enthalpy balance is

$$\Delta h^\circ (T_{final}) = \sum_{i_{product}}^{I_{product}} n_{i_{product}} h_{i_{product}}^\circ (T_{final}) - \sum_{i_{reactant}}^{I_{reactant}} n_{i_{reactant}} h_{i_{reactant}}^\circ (T_{initial_{i_{reactant}}}). \quad (9.51)$$

So for example, to determine the heat of formation of  $CO_2$  at 1000 K where the initial reactants are also at 1000 K, the calculation would be

$$\begin{aligned} \Delta h_{fCO_2}^\circ (1000) = & \\ & \left( \Delta h_{fCO_2}^\circ (298.15) + \left\{ h_{fCO_2}^\circ (1000) - h_{fCO_2}^\circ (298.15) \right\} \right) - \\ & \left( \Delta h_{fC(s)}^\circ (298.15) + \left\{ h_{fC(s)}^\circ (1000) - h_{fC(s)}^\circ (298.15) \right\} \right) - \\ & \left( \Delta h_{fO_2}^\circ (298.15) + \left\{ h_{fO_2}^\circ (1000) - h_{fO_2}^\circ (298.15) \right\} \right). \end{aligned} \quad (9.52)$$

Putting in the numbers from tabulated data gives

$$\Delta h_{fCO_2}^\circ (1000) = [-393.522 + 33.397] - [0 + 11.795] - [0 + 22.703] = -394.623. \quad (9.53)$$

which is the tabulated value of the heat of formation of carbon dioxide at 1000 K. See Appendix 2 in the AA283 course reader. Note that the enthalpy of the reference reactants at the reaction temperature must be included in the calculation of the heat of formation calculation. Further discussion of heats of formation can be found in Appendix 1 of the AA283 course reader and tables of thermo-chemical data for selected species can be found in Appendix 2.

## 9.6 Chemical equilibrium, the method of element potentials

If the species are allowed to react at constant temperature and pressure, the mole fractions will evolve toward values that minimize the extensive Gibbs free energy of the system

subject to the constraint that the number of moles of each element in the mixture remains fixed. The number of moles of each atom in the system is given by

$$a_j = \sum_{i=1}^I n_i A_{ij} \quad (9.54)$$

where  $A_{ij}$  is the number of atoms of the  $j$ th element in the  $i$ th molecular species. The appropriate picture of our system is shown in Figure 9.3. The Gibbs free energy of the system is

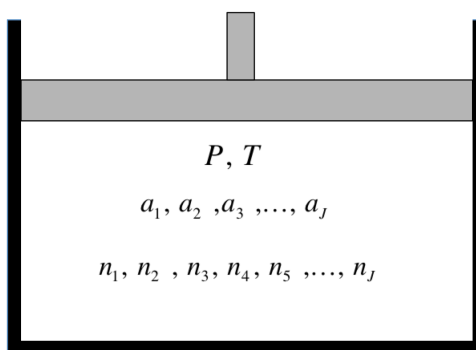


Figure 9.3: System of gas phase reacting molecular species at constant temperature and pressure with fixed number of moles of each element.

$$G(T, P, n_1, n_2, \dots, n_I) = \sum_{i=1}^I x_i g_i(T, P, x_i) \quad (9.55)$$

Written out

$$G(T, P, n_1, n_2, \dots, n_I) = N \sum_{i=1}^I x_i (g_i^\circ(T) + R_u T \ln(x_i)) + N R_u T \ln\left(\frac{P}{P^\circ}\right) \quad (9.56)$$

We will use the method of Lagrange multipliers to minimize the Gibbs free energy subject to the atom constraints. Minimize the function

$$W(T, P, n_1, n_2, \dots, n_I, \lambda_1, \dots, \lambda_J) = G(T, P, n_1, n_2, \dots, n_I) - R_u T \sum_{j=1}^J \lambda_j \left( \sum_{i=1}^I n_i A_{ij} - a_j \right) \quad (9.57)$$

where the  $J$  unknown Lagrange multipliers,  $\lambda_j$ , are dimensionless. Our modified equilibrium condition is

$$dW = \frac{\partial W}{\partial T} dT + \frac{\partial W}{\partial P} dP + \frac{\partial W}{\partial n_1} dn_1 + \dots + \frac{\partial W}{\partial n_I} dn_I + \frac{\partial W}{\partial \lambda_1} d\lambda_1 + \dots + \frac{\partial W}{\partial \lambda_J} d\lambda_J = 0 \quad (9.58)$$

Substitute (9.57) into (9.58) and impose  $dP = dT = 0$ .

$$dW = \sum_{i=1}^I (n_i dg_i(T, P, x_i) + g_i(T, P, x_i) dn_i) - R_u T \sum_{j=1}^J \lambda_j \sum_{i=1}^I dn_i A_{ij} \quad (9.59)$$

The order of the sums can be rearranged so (9.59) can be written as

$$dW = \sum_{i=1}^I n_i dg_i(T, P, x_i) + \sum_{i=1}^I \left( g_i(T, P, x_i) - R_u T \sum_{j=1}^J \lambda_j A_{ij} \right) dn_i = 0. \quad (9.60)$$

The differential of the molar Gibbs free energy is

$$dg_i = \frac{\partial g_i}{\partial T} dT + \frac{\partial g_i}{\partial P} dP + R_u T \frac{dx_i}{x_i}. \quad (9.61)$$

For a process that takes place at constant temperature and pressure

$$dW = R_u T \sum_{i=1}^I n_i \frac{dx_i}{x_i} + \sum_{i=1}^I \left( g_i(T, P, x_i) - R_u T \sum_{j=1}^J \lambda_j A_{ij} \right) dn_i = 0. \quad (9.62)$$

The first sum in (9.62) can be re-written as follows

$$dW = R_u T N \sum_{i=1}^I x_i \frac{dx_i}{x_i} + \sum_{i=1}^I \left( g_i(T, P, x_i) - R_u T \sum_{j=1}^J \lambda_j A_{ij} \right) dn_i = 0 \quad (9.63)$$

or

$$dW = R_u T N \sum_{i=1}^I dx_i + \sum_{i=1}^I \left( g_i(T, P, x_i) - R_u T \sum_{j=1}^J \lambda_j A_{ij} \right) dn_i = 0. \quad (9.64)$$



But the normalization conditions for the sum of the mole fractions implies that

$$\sum_{i=1}^I dx_i = d\left(\sum_{i=1}^I x_i\right) = d(1) = 0. \quad (9.65)$$

Finally our modified equilibrium condition is

$$dW = \sum_{i=1}^I \left( g_i(T, P, x_i) - R_u T \sum_{j=1}^J \lambda_j A_{ij} \right) dn_i = 0 \quad (9.66)$$

Since the  $dn_i$  are completely free, the condition (9.66) can only be satisfied if

$$g_i(T, P, x_i) = R_u T \sum_{j=1}^J \lambda_j A_{ij}. \quad (9.67)$$

The Gibbs free energy of the system is

$$G(T, P, n_1, n_2, \dots, n_I) = R_u T \sum_{i=1}^I \sum_{j=1}^J n_i \lambda_j A_{ij}. \quad (9.68)$$

Each atom in the mixture contributes equally to the extensive Gibbs free energy regardless of which molecule it is in. The molar Gibbs free energy of the  $i$ th gas phase species is

$$g_i(T, P, x_i) = g_i^\circ(T) + R_u T \ln(x_i) + R_u T \ln\left(\frac{P}{P^\circ}\right). \quad (9.69)$$

Insert (9.69) into (9.67). For each gas phase species

$$\frac{g_i^\circ(T)}{R_u T} + \ln(x_i) + \ln\left(\frac{P}{P^\circ}\right) = \sum_{j=1}^J \lambda_j A_{ij}. \quad (9.70)$$

Solve for the mole fraction of the  $i$ th species in the mixture.

$$x_i = \text{Exp} \left\{ -\frac{g_i^\circ(T)}{R_u T} - \ln\left(\frac{P}{P^\circ}\right) + \sum_{j=1}^J \lambda_j A_{ij} \right\}. \quad (9.71)$$

The constraints on the atoms are

$$a_j = \sum_{i=1}^I x_i A_{ij}. \quad (9.72)$$

Substitute (9.71) into (9.72).

$$a_j = N \sum_{i=1}^I A_{ij} \text{Exp} \left\{ -\frac{g_i^\circ(T)}{R_u T} - \ln \left( \frac{P}{P^\circ} \right) + \sum_{j_1=1}^J \lambda_j A_{ij_1} \right\} \quad j = 1, \dots, J \quad (9.73)$$

Note that we have to introduce the dummy index  $j_1$  in the formula for  $x_i$  when we make the substitution. The normalization condition on the mole fractions gives

$$\left\{ -\frac{g_i^\circ(T)}{R_u T} - \ln \left( \frac{P}{P^\circ} \right) + \sum_{j_1=1}^J \lambda_j A_{ij_1} \right\} = 1 \quad (9.74)$$

The total number of moles in the mixture is  $N$ . Equations, (9.73), and (9.74) are  $J + 1$  equations in the unknowns  $\lambda_1, \dots, \lambda_J$ , and  $N$ .

As a practical matter, it is easier to compute the solution to equations (9.73) and (9.74) by reformulating the equations to get rid of the exponentials. Define

$$B_i(T) \equiv \text{Exp} \left\{ -\frac{g_i^\circ(T)}{R_u T} \right\} \quad (9.75)$$

In addition, define

$$y_j = \text{Exp}(\lambda_j). \quad (9.76)$$

The mole fractions become

$$x_i = \left( \frac{P^\circ}{P} \right) B_i \prod_{j_1=1}^J (y_{j_1})^{A_{ij_1}} \quad (9.77)$$

The system of equations that needs to be solved now becomes

$$\begin{aligned} \left(\frac{P^\circ}{P}\right) N \sum_{i=1}^I A_{ij} B_i \prod_{j_1=1}^J (y_{j_1})^{A_{ij_1}} &= a_j, \quad j = 1, \dots, J \\ \left(\frac{P^\circ}{P}\right) \sum_{i=1}^I B_i \prod_{j=1}^J (y_j)^{A_{ij}} &= 1 \end{aligned} \tag{9.78}$$

Note that in this formulation only the always positive  $y_j$  are needed to determine the mole fractions. The element potentials  $\lambda_j$ , which are the logarithm of the  $y_j$ , never actually need to be calculated.

A key advantage of this formulation of the problem is that the equations that need to be solved for the unknown  $y_i$  and  $N$  are multivariate polynomials, and algorithms are available that enable the roots to be determined without requiring an initial guess of the solution. Typically a number of real and complex roots are returned. The correct root is the one with all positive real values of the  $y_i$  and  $N$ . In general, there is only one such root.

## 9.7 Example - combustion of carbon monoxide

If we mix carbon monoxide ( $CO$ ) and oxygen ( $O_2$ ) at  $10^5 Pa$  and  $298.15 K$  then ignite the mixture, the result is a strongly exothermic reaction. The simplest model of such a reaction takes one mole of  $CO$  plus half a mole of  $O_2$  to produce one mole of carbon dioxide.



But this model is not very meaningful without some information about the temperature of the process. If the reaction occurs in an adiabatic system at constant pressure, the final temperature is very high and at that temperature the hot gas consists of a mixture of a number of species beside  $CO_2$ . A more realistic model assumes that the composition includes virtually all of the combinations of carbon and oxygen that one can think of including



Other more complex molecules are possible such as  $C_2$  and  $O_3$  but are only present in extraordinarily low concentrations. For the composition (9.79) the temperature of the

mixture at one atmosphere turns out to be  $2975.34\text{ K}$ . This is called the adiabatic flame temperature.

Let's use the minimization of the Gibbs free energy to determine the relative concentrations of each molecular species for the mixture (9.80) at the equilibrium temperature  $2975.34\text{ K}$ . We will order the species as in (9.80). All the species are in the gas phase and the matrix of element coefficients  $A_{ij}$  is shown in Figure 9.4.

	Atom	C	O
Molecule		$j=1$	$j=2$
C	$i=1$	1	0
CO	$i=2$	1	1
CO <sub>2</sub>	$i=3$	1	2
O	$i=4$	0	1
O <sub>2</sub>	$i=5$	0	2

Figure 9.4: Matrix of element coefficients for the CO, O<sub>2</sub> system.

For this system of molecular species, (9.73) and (9.74) lead to the following equations governing the mole fractions and the total number of moles. Note that  $P = P^\circ$  in this case.

$$\begin{aligned}
 a_1 = N & \left( A_{11} \text{Exp} \left( -\frac{g_1^\circ}{R_u T} + \lambda_1 A_{11} + \lambda_2 A_{12} \right) + A_{21} \text{Exp} \left( -\frac{g_2^\circ}{R_u T} + \lambda_1 A_{21} + \lambda_2 A_{22} \right) + \right. \\
 & A_{31} \text{Exp} \left( -\frac{g_3^\circ}{R_u T} + \lambda_1 A_{31} + \lambda_2 A_{32} \right) + A_{41} \text{Exp} \left( -\frac{g_4^\circ}{R_u T} + \lambda_1 A_{41} + \lambda_2 A_{42} \right) + \\
 & \left. A_{51} \text{Exp} \left( -\frac{g_5^\circ}{R_u T} + \lambda_1 A_{51} + \lambda_2 A_{52} \right) \right)
 \end{aligned} \tag{9.81}$$

$$\begin{aligned}
 a_2 = N & \left( A_{12} \text{Exp} \left( -\frac{g_1^\circ}{R_u T} + \lambda_1 A_{11} + \lambda_2 A_{12} \right) + A_{22} \text{Exp} \left( -\frac{g_2^\circ}{R_u T} + \lambda_1 A_{21} + \lambda_2 A_{22} \right) + \right. \\
 & A_{32} \text{Exp} \left( -\frac{g_3^\circ}{R_u T} + \lambda_1 A_{31} + \lambda_2 A_{32} \right) + A_{42} \text{Exp} \left( -\frac{g_4^\circ}{R_u T} + \lambda_1 A_{41} + \lambda_2 A_{42} \right) + \\
 & \left. A_{52} \text{Exp} \left( -\frac{g_5^\circ}{R_u T} + \lambda_1 A_{51} + \lambda_2 A_{52} \right) \right)
 \end{aligned} \tag{9.82}$$

$$\begin{aligned}
1 = & \text{Exp} \left( -\frac{g_1^\circ}{R_u T} + \lambda_1 A_{11} + \lambda_2 A_{12} \right) + \text{Exp} \left( -\frac{g_2^\circ}{R_u T} + \lambda_1 A_{21} + \lambda_2 A_{22} \right) + \\
& \text{Exp} \left( -\frac{g_3^\circ}{R_u T} + \lambda_1 A_{31} + \lambda_2 A_{32} \right) + \text{Exp} \left( -\frac{g_4^\circ}{R_u T} + \lambda_1 A_{41} + \lambda_2 A_{42} \right) + \\
& \text{Exp} \left( -\frac{g_5^\circ}{R_u T} + \lambda_1 A_{51} + \lambda_2 A_{52} \right)
\end{aligned} \tag{9.83}$$

The unknowns in this system are the two Lagrange multipliers  $\lambda_1$  and  $\lambda_2$  corresponding to each element in the mixture and the total number of moles. The number of moles of carbon atoms is  $a_1 = 1$  and the number of moles of oxygen atoms is  $a_2 = 2$ . The great advantage of this method is that the number of unknowns is limited to the number of elements in the mixture not the number of molecular species. Use (9.75) and (9.76) to rewrite (9.81), (9.82) and (9.83) in the form of (9.78).

$$\begin{aligned}
a_1 = & N(A_{11}B_1y_1^{A_{11}}y_2^{A_{12}} + A_{21}B_2y_1^{A_{21}}y_2^{A_{22}} + A_{31}B_3y_1^{A_{31}}y_2^{A_{32}} + \\
& A_{41}B_4y_1^{A_{41}}y_2^{A_{42}} + A_{51}B_5y_1^{A_{51}}y_2^{A_{52}})
\end{aligned} \tag{9.84}$$

$$\begin{aligned}
a_2 = & N(A_{12}B_1y_1^{A_{11}}y_2^{A_{12}} + A_{22}B_2y_1^{A_{21}}y_2^{A_{22}} + A_{32}B_3y_1^{A_{31}}y_2^{A_{32}} + \\
& A_{42}B_4y_1^{A_{41}}y_2^{A_{42}} + A_{52}B_5y_1^{A_{51}}y_2^{A_{52}})
\end{aligned} \tag{9.85}$$

$$\begin{aligned}
1 = & B_1y_1^{A_{11}}y_2^{A_{12}} + B_2y_1^{A_{21}}y_2^{A_{22}} + B_3y_1^{A_{31}}y_2^{A_{32}} + \\
& B_4y_1^{A_{41}}y_2^{A_{42}} + B_5y_1^{A_{51}}y_2^{A_{52}}
\end{aligned} \tag{9.86}$$

Substitute the  $A_{ij}$  in equations (9.84), (9.85) and (9.86).

$$1 = N (B_1y_1 + B_2y_1y_2 + B_3y_1y_2^2) \tag{9.87}$$

$$2 = N (B_2y_1y_2 + 2B_3y_1y_2^2 + B_4y_2 + 2B_5y_2^2) \tag{9.88}$$

$$1 = B_1y_1 + B_2y_1y_2 + B_3y_1y_2^2 + B_4y_2 + B_5y_2^2 \tag{9.89}$$

The  $B$  coefficients are

$$\begin{aligned}
 B_1 &= e^{-\frac{g_C^\circ}{R_u T}} \\
 B_2 &= e^{-\frac{g_{CO}^\circ}{R_u T}} \\
 B_3 &= e^{-\frac{g_{CO_2}^\circ}{R_u T}} \\
 B_4 &= e^{-\frac{g_O^\circ}{R_u T}} \\
 B_5 &= e^{-\frac{g_{O_2}^\circ}{R_u T}}.
 \end{aligned} \tag{9.90}$$

At this point we need to use tabulated thermodynamic data to evaluate the  $B$  coefficients. The Gibbs free energy of the  $i$ th molecular species is

$$g_i^\circ(T) = \Delta h_{fi}^\circ(T_{ref}) + \{h_i^\circ(T) - h_i^\circ(T_{ref})\} - T s_i^\circ(T). \tag{9.91}$$

Data for each species is as follows (See appendix 2 of the AA283 course reader). In the same order as (9.80)

$$\begin{aligned}
 g_C^\circ(2975.34) &= 715.004 + 56.208 - 2975.34(0.206054) = 158.131 \text{ kJ/mole} \\
 g_{CO}^\circ(2975.34) &= -110.541 + 92.705 - 2975.34(0.273228) = -830.782 \text{ kJ/mole} \\
 g_{CO_2}^\circ(2975.34) &= -393.522 + 151.465 - 2975.34(0.333615) = -1234.68 \text{ kJ/mole} \\
 g_O^\circ(2975.34) &= 249.195 + 56.1033 - 2975.34(0.209443) = -317.866 \text{ kJ/mole} \\
 g_{O_2}^\circ(2975.34) &= 0.00 + 97.1985 - 2975.34(0.284098) = -748.09 \text{ kJ/mole}.
 \end{aligned} \tag{9.92}$$

The universal gas constant in appropriate units is

$$R_u = 8.314472 \times 10^{-3} \text{ kJ/mole} - K \tag{9.93}$$

and  $R_u T = 24.7384 \text{ kJ/mole}$ . Now the coefficients are

$$\begin{aligned}
 B_1 &= \text{Exp} \left( -\frac{g_C^\circ}{R_u T} \right) = \text{Exp} \left( -\frac{158.131}{24.7382} \right) = 1.67346 \times 10^{-3} \\
 B_2 &= \text{Exp} \left( -\frac{g_{CO}^\circ}{R_u T} \right) = \text{Exp} \left( \frac{830.782}{24.7382} \right) = 3.84498 \times 10^{14} \\
 B_3 &= \text{Exp} \left( -\frac{g_{CO_2}^\circ}{R_u T} \right) = \text{Exp} \left( \frac{1234.68}{24.7382} \right) = 4.73778 \times 10^{21} \\
 B_4 &= \text{Exp} \left( -\frac{g_O^\circ}{R_u T} \right) = \text{Exp} \left( \frac{317.866}{24.7382} \right) = 3.80483 \times 10^5 \\
 B_5 &= \text{Exp} \left( -\frac{g_{O_2}^\circ}{R_u T} \right) = \text{Exp} \left( \frac{748.090}{24.7382} \right) = 1.35889 \times 10^{13}.
 \end{aligned} \tag{9.94}$$

I used Mathematica to solve the system, (9.87), (9.88), and (9.89). The result is

$$\begin{aligned}
 y_1 &= 1.42474 \times 10^{-11} \\
 y_2 &= 0.392402 \\
 N &= 1.24144
 \end{aligned} \tag{9.95}$$

At the mixture temperature  $T = 2975.34 \text{ K}$ , the mole fractions of the various species are

$$\begin{aligned}
 x_C &= B_1 y_1 = 1.42474 \times 10^{-11} \\
 x_{CO} &= B_2 y_1 y_2 = 6.23285 \times 10^{10} \times 1.42474 \times 10^{-11} \times 0.392402 = 0.34846 \\
 x_{CO_2} &= B_3 y_1 y_2^2 = 2.08341 \times 10^{11} \times 1.42474 \times 10^{-11} \times 0.392402^2 = 0.45706 \\
 x_O &= B_4 y_2 = 0.103215 \times 0.392402 = 0.0405018 \\
 x_{O_2} &= B_5 y_2^2 = 0.392402^2 = 0.153979.
 \end{aligned} \tag{9.96}$$

Note that there is almost no free carbon at this temperature. We could have dropped  $C$  from the mixture (9.80) and still gotten practically the same result.

### 9.7.1 Adiabatic flame temperature

In the example in the previous section the products of combustion were evaluated at the adiabatic flame temperature. This can be defined at constant volume or constant pressure. For our purposes we will use the adiabatic flame temperature at constant pressure. Imagine the reactants brought together in a piston-cylinder combination permitting the volume to be adjusted to keep the pressure constant as the reaction proceeds. A source of ignition is used to start the reaction that evolves to the equilibrium state defined by the equilibrium

species concentrations at the original pressure and at an elevated temperature called the adiabatic flame temperature. In the process the Gibbs function is minimized and since the process is adiabatic, the enthalpy before and after the reaction is the same.

The general enthalpy balance for a reaction is given in (9.51). Fully written out the balance is

$$\Delta h^\circ(T_{final}) = \sum_{i_{product}}^{I_{product}} n_{i_{product}} \left\{ \Delta h_{f i_{product}}^\circ(298.15) + \left( h_{i_{product}}^\circ(T_{final}) - h_{i_{product}}^\circ(298.15) \right) \right\} - \sum_{i_{reactant}}^{I_{reactant}} n_{i_{reactant}} \left\{ \Delta h_{f i_{reactant}}^\circ(298.15) + \left( h_{i_{reactant}}^\circ(T_{i_{reactant}}) - h_{i_{reactant}}^\circ(298.15) \right) \right\}. \quad (9.97)$$

If the reaction takes place adiabatically then  $\Delta h^\circ(T_{final}) = 0$  and

$$\sum_{i_{product}}^{I_{product}} n_{i_{product}} \left\{ \Delta h_{f i_{product}}^\circ(298.15) + \left( h_{i_{product}}^\circ(T_{final}) - h_{i_{product}}^\circ(298.15) \right) \right\} = \sum_{i_{reactant}}^{I_{reactant}} n_{i_{reactant}} \left\{ \Delta h_{f i_{reactant}}^\circ(298.15) + \left( h_{i_{reactant}}^\circ(T_{i_{reactant}}) - h_{i_{reactant}}^\circ(298.15) \right) \right\}. \quad (9.98)$$

Equation (9.98) can be solved along with (9.87), (9.88) and (9.89) to determine the final temperature of the mixture along with the mole fractions and total number of moles. In the carbon monoxide combustion example of the previous section we would write

$$\begin{aligned} & n_C \left\{ \Delta h_{f C}^\circ(298.15) + \left( h_C^\circ(T_{final}) - h_C^\circ(298.15) \right) \right\} + \\ & n_{CO} \left\{ \Delta h_{f CO}^\circ(298.15) + \left( h_{CO}^\circ(T_{final}) - h_{CO}^\circ(298.15) \right) \right\} + \\ & n_{CO_2} \left\{ \Delta h_{f CO_2}^\circ(298.15) + \left( h_{CO_2}^\circ(T_{final}) - h_{CO_2}^\circ(298.15) \right) \right\} + \\ & n_O \left\{ \Delta h_{f O}^\circ(298.15) + \left( h_O^\circ(T_{final}) - h_O^\circ(298.15) \right) \right\} + \\ & n_{O_2} \left\{ \Delta h_{f O_2}^\circ(298.15) + \left( h_{O_2}^\circ(T_{final}) - h_{O_2}^\circ(298.15) \right) \right\} = \\ & n_{CO} \left\{ \Delta h_{f CO}^\circ(298.15) \right\} + n_{O_2} \left\{ \Delta h_{f O_2}^\circ(298.15) \right\}. \end{aligned} \quad (9.99)$$

The enthalpy of the reactants is

$$\begin{aligned} & n_{CO} \left\{ \Delta h_{f CO}^\circ(298.15) \right\} + n_{O_2} \left\{ \Delta h_{f O_2}^\circ(298.15) \right\} = \\ & 1.0 \text{ kgmole} \left\{ -110.527 \times 10^3 \text{ kJ/kgmole} \right\} + 0.5 \text{ kgmole} \left\{ 0 \text{ kJ/kgmole} \right\} = \\ & -110.527 \times 10^3 \text{ kJ}. \end{aligned} \quad (9.100)$$



On a per unit mass basis the enthalpy of the reactant mixture is

$$\frac{-110.527 \times 10^6 J}{1 \times 28.014 + 0.5 \times 31.98} = -2.5117 \times 10^6 J/kg. \quad (9.101)$$

The enthalpy per unit mass of the product mixture at various temperatures is plotted in Figure 9.5.

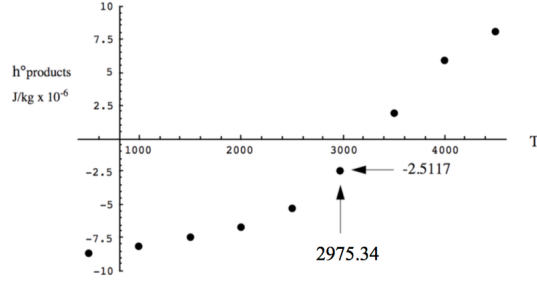


Figure 9.5: *Enthalpy of the product mixture as a function of temperature.*

As the products of combustion are cooled from 4000 K the enthalpy decreases monotonically. The only temperature where the enthalpy of the product mixture matches that of the original reactants is the adiabatic flame temperature, 2975.34 K.

### 9.7.2 Isentropic expansion

Now consider an isentropic expansion from a known initial state,  $(T_{initial}, P_{initial})$  to a final state  $(T_{final}, P_{final})$  with the final pressure known. The condition that determines the temperature of the final state is

$$S(T_{final}, P_{final}, n_{1_{final}}, n_{2_{final}}, n_{3_{final}}, \dots, n_{I_{final}}) = S(T_{initial}, P_{initial}, n_{1_{initial}}, n_{2_{initial}}, n_{3_{initial}}, \dots, n_{I_{initial}}) \quad (9.102)$$

or

$$\sum_{i=1}^I n_{i_{final}} s_i^\circ(T_{final}) - N_{final} R_u \sum_{i=1}^I x_{i_{final}} \ln(x_{i_{final}}) - N_{final} R_u \ln\left(\frac{P_{final}}{P^\circ}\right) = \sum_{i=1}^I n_{i_{initial}} s_i^\circ(T_{initial}) - N_{initial} R_u \sum_{i=1}^I x_{i_{initial}} \ln(x_{i_{initial}}) - N_{initial} R_u \ln\left(\frac{P_{initial}}{P^\circ}\right). \quad (9.103)$$

Equation (9.103) can be solved along with (9.87), (9.88) and (9.89) to determine the final temperature of the mixture after isentropic expansion along with the mole fractions and total number of moles.

For example, take the mixture from the previous section at the initial state,  $T_{initial} = 2975.34 K$  and  $P_{initial} = 1 bar$ . The entropy of the system on a per unit mass basis is  $8.7357 kJ/kg-K$  which is essentially equivalent to the extensive entropy. Now expand the mixture to  $P_{final} = 0.1 bar$ . If we calculate the entropy of the system at this pressure and various temperatures, the result is the following plot.

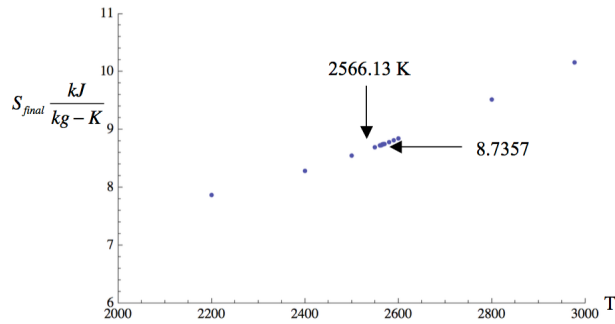


Figure 9.6: Entropy of the product mixture as a function of temperature.

The temperature at which the entropy of the final state is the same as the initial state is  $T_{final} = 2566.13 K$ .

### 9.7.3 Nozzle expansion

If we interpret the expansion just described as an adiabatic, isentropic expansion in a nozzle we can use the conservation of stagnation enthalpy to determine the speed of the gas mixture at the end of the expansion.

$$H_{initial} = H_{final} + \frac{1}{2}U^2 \quad (9.104)$$

The initial enthalpy is taken to be the reservoir value. For this example the numbers are

$$U = \sqrt{2(H_{initial} - H_{final})} = \sqrt{2(-2.51162 + 3.94733) \times 10^6 J/kg} = 1694.53 m/sec. \quad (9.105)$$

Ordinarily we are given the geometric area ratio of the nozzle rather than the pressure ratio. Determining the exit velocity in this case is a little more involved. Here we need to carry out a series of calculations at constant entropy and varying final pressure. For each calculation we need to determine the density and velocity of the mixture and plot the product  $\rho U$  as a function of the pressure ratio. Beginning with the mixture at the adiabatic flame temperature as the reservoir condition, the results are plotted below.

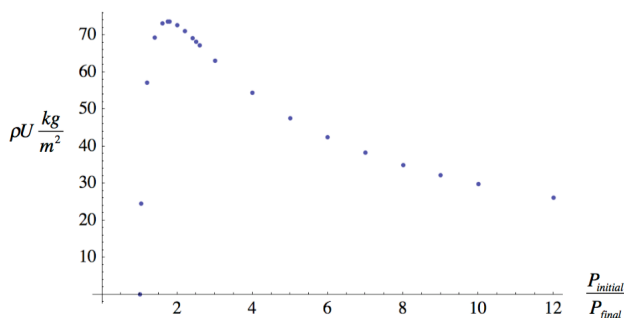


Figure 9.7: *Mass flux in a converging-diverging nozzle as a function of nozzle static pressure ratio.*

The maximum mass flux occurs at the nozzle throat. Equate the mass flow at the throat and the nozzle exit. For  $P_{initial}/P_{final} = 10.0$  the nozzle area ratio is

$$\frac{A_e}{A_t} = \frac{\rho_t U_t}{\rho_e U_e} = \frac{73.6768}{29.8354} = 2.46944. \quad (9.106)$$

This completes the specification of the nozzle flow. The case we have considered here is called the shifting equilibrium case where the gas mixture is at equilibrium at every point in the nozzle. One can also consider the case of frozen flow where the composition of the gas mixture is held fixed at the reservoir condition.

## 9.8 Rocket performance using CEA

The equilibrium combustion package CEA (Chemical Equilibrium with Applications) from NASA Glenn can also be used to perform equilibrium chemistry calculations and has a capability similar to STANJAN but with a much wider range of chemicals with data based on the current standard pressure. Some typical performance parameters for several propellant combinations at two chamber pressures are shown in Figure 9.8. The propellants are taken to be at an equivalence ratio of one (complete consumption of fuel and oxidizer) and so the exhaust velocity is not optimized. The numbers correspond to the effective

exhaust velocity for the given chamber pressure and area ratio assuming vacuum ambient pressure. The maximum effective exhaust velocity generally occurs with a somewhat fuel rich mixture that produces more low molecular weight species in the exhaust stream.

Propellants	$P_{chamber}$ bar	$T_{chamber}$ K	$C^*$ M/Sec	$C_e _{A_e/A_t = 100}$ M/Sec	$C_e _{A_e/A_t \rightarrow \infty}$ M/Sec
$H_2 + \frac{1}{2}O_2$	50	3626	2186	4541	5285
	100	3730	2203	4562	5287
$N_2H_4 + \frac{1}{2}N_2O_4$	50	3379	1818	3637	4030
	100	3451	1829	3643	4032
$(1.0)RP - 1 + (3.4)O_2$ <i>by mass</i>	50	3676	1733	3631	4467
	100	3787	1749	3654	4469
$(0.1)Al + (0.835)NH_4ClO_4$ $+ (0.065)C_6H_6$ <i>by mass</i>	50	3434	1511	3160	3726
	100	3514	1520	3171	3728

Figure 9.8: Some typical performance parameters for several propellant combinations at two chamber pressures.