Properties of Mixtures

John W Daily

Mixtures of Ideal Gases

Mole fractions $$x_i \equiv \frac{N_i}{N_{tot}} = \frac{n_i}{n_{tot}} \qquad \sum_i \mathrm{x_i} = 1$$

Mass fractions $$y_i \equiv \frac{m_i}{m_{tot}} \qquad \sum_i \mathrm{y_i} = 1$$

$$y_i = x_i \frac{MW_i}{MW_{mix}} \qquad x_i = y_i \frac{MW_{mix}}{MW_i}$$

$$MW_{mix} = \sum_i x_i MW_i = \frac{1}{\sum_i (y_i / MW_i)}$$

Partial pressures $$p_i = x_i \mathrm{p} \qquad p = \sum_i p_i$$

Energy Referencing

- The issue with mixtures is energy referencing. The usual method is to reference the enthalpy using the "enthalpy of formation." This is the enthalpy referenced to the "standard reference state."
- The usual notation is $\Delta_f H^o$, or $\bar{h}_f^0$
- So the enthalpy is

$$\bar{h}_i(T) = \bar{h}_{f,i}^0 + (\bar{h}_i(T) - \bar{h}_i(298.15))$$

Where the last term accounts for the change in enthalpy from the standard reference state

The Standard Reference State

- For liquids and solids, the standard state is the thermodynamically stable state at a pressure of 1 atm and a specified temperature. The stable state could be liquid or solid.
- For gases, the standard state is the gaseous state at a pressure of 1 atm and a specified temperature, based on the assumption of ideal gas behavior.
- For dissolved species, the standard state is a 1 M solution at a pressure of 1 atm and specified temperature, based on the assumption of ideal solution behavior.

Mixture internal energy/enthapy $h = u + pv$

$$u_{mix} = \sum_i y_i u_i \qquad h_{mix} = \sum_i y_i h_i$$

$$\bar{u}_{mix} = \sum_i x_i \bar{u}_i \qquad \bar{h}_{mix} = \sum_i x_i \bar{h}_i$$

How to reference internal energy and enthalpies of each species wrt each other:

$$\bar{u}_i(T) = \bar{u}^0_{f,i} + \Delta\bar{u}_i(T) \qquad \bar{h}_i(T) = \bar{h}^0_{f,i} + \Delta\bar{h}_i(T)$$

$\bar{u}^0_{f,i}$ $\bar{h}^0_{f,i}$ are the internal energy/enthalpy of formation defined at a standard reference state.

$$T_{ref} = 25\text{C} = 298.15\text{K}$$

$$p_{ref} = 1\ \text{Atm} = 101325\ \text{Pa}$$

And the enthalpies of formation are zero for the elements in their naturally occurring state at the reference state conditions.

Note that:

$$\Delta\bar{u}_i(T) = \bar{u}_i(T) - \bar{u}_i(T_0) = \int_{T_0}^{T} c_v dT$$

$$\Delta\bar{h}_i(T) = \bar{h}_i(T) - \bar{h}_i(T_0) = \int_{T_0}^{T} c_p dT$$

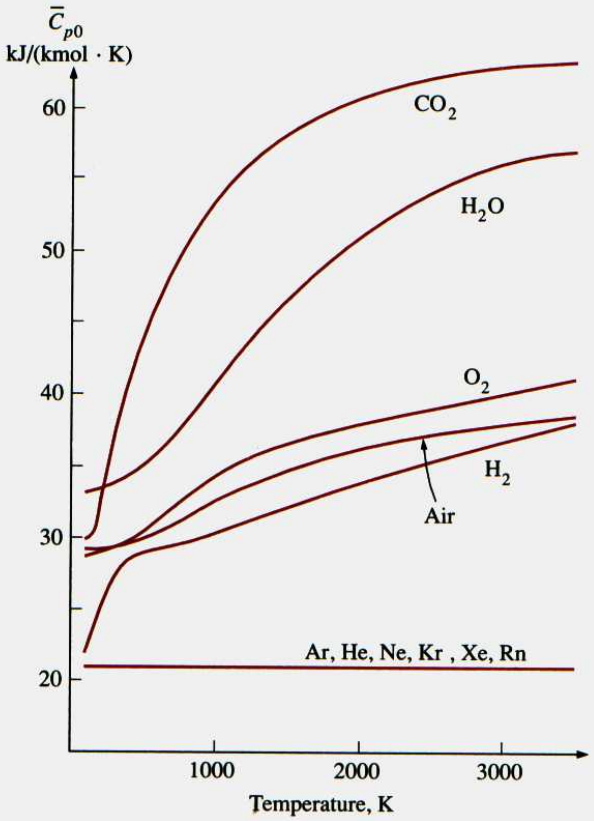


FIGURE 3-76
Ideal-gas constant-pressure specific heats for some gases (see Table A-2*c* for $\bar{C}_{p0}$ equations).

Mixture entropy

- We have to be careful with entropy because it is a function of both temperature and pressure.
- Therefore, use the partial pressure when evaluating the component entropy.

$$s_{mix}(T,p) = \sum_i y_i s_i(T,p_i)$$

$$\bar{s}_{mix}(T,p) = \sum_i x_i \bar{s}_i(T,p_i)$$

Reactant and Product Mixtures

Stoichiometry - The reaction balance equation is a statement of conservation of mass.

$$C_x H_y + a(O_2 + 3.76N_2) \rightarrow xCO_2 + (y/2)H_2O + 3.76aN_2$$

$$a = x + y/4$$

This, of course, is a global reaction. But the conservation concept applies to elementary reactions.

In combustion, the mixture of fuel and oxidizer that results in complete combustion is called the stoichiometric mixture.

Enthalpy of Formation Data

- Tabulated in a number of sources, in particular in the NIST database: janaf.nist.gov

Carbon Dioxide (CO_2) $C_1O_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1}\ mol^{-1}$				$kJ \cdot mol^{-1}$		
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	-9.364	-393.151	-393.151	INFINITE
100	29.208	179.009	243.568	-6.456	-393.208	-393.683	205.639
200	32.359	199.975	217.046	-3.414	-393.404	-394.085	102.924
298.15	37.129	213.795	213.795	0.	-393.522	-394.389	69.095
300	37.221	214.025	213.795	0.069	-393.523	-394.394	68.670
400	41.325	225.314	215.307	4.003	-393.583	-394.675	51.539
500	44.627	234.901	218.290	8.305	-393.666	-394.939	41.259
600	47.321	243.283	221.772	12.907	-393.803	-395.182	34.404
700	49.564	250.750	225.388	17.754	-393.983	-395.398	29.505
800	51.434	257.494	228.986	22.806	-394.188	-395.586	25.829
900	52.999	263.645	232.500	28.030	-394.405	-395.748	22.969
1000	54.308	269.299	235.901	33.397	-394.623	-395.886	20.679

Various Ratios

- Air/Fuel Ratio $\dfrac{m_{air}}{m_{fuel}}$ or $\dfrac{\mathrm{N_{air}}}{\mathrm{N_{fuel}}}$

- Equivalence Ratio

$$\phi = \frac{(A/F)_{stoic}}{(A/F)} = \frac{(F/A)}{(F/A)_{stoic}}$$

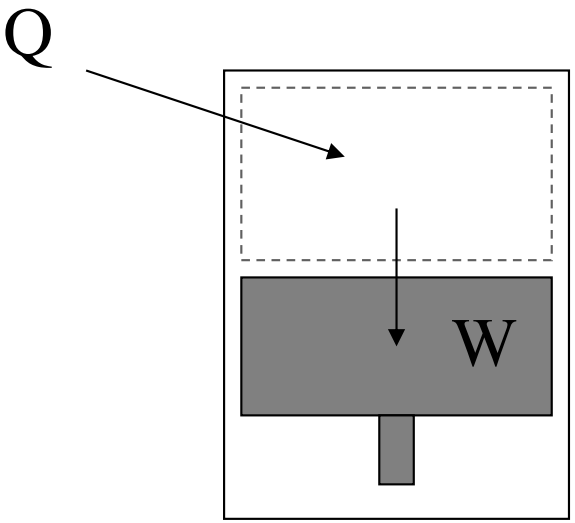
Just make sure you know whether mass or moles are being used!

First Law Analysis

- Control Mass (Change in Time)

$$E_2 - E_1 = Q_{in} - W_{out}$$

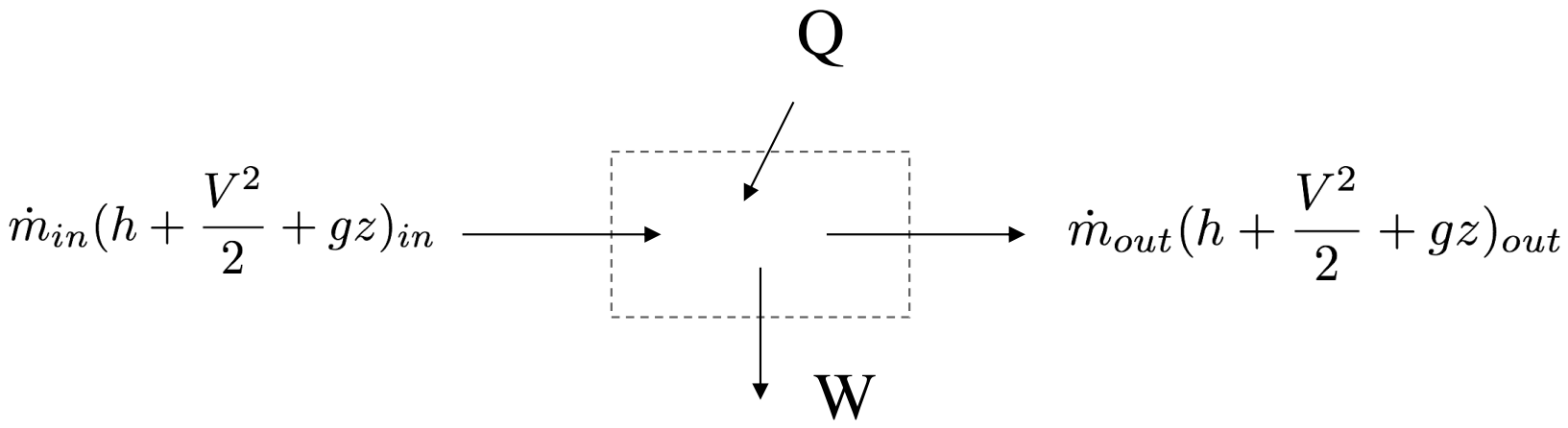
$$E = m(u + \frac{1}{2}V^2 + gz)$$



First Law Analysis

- Control Volume (Steady State)

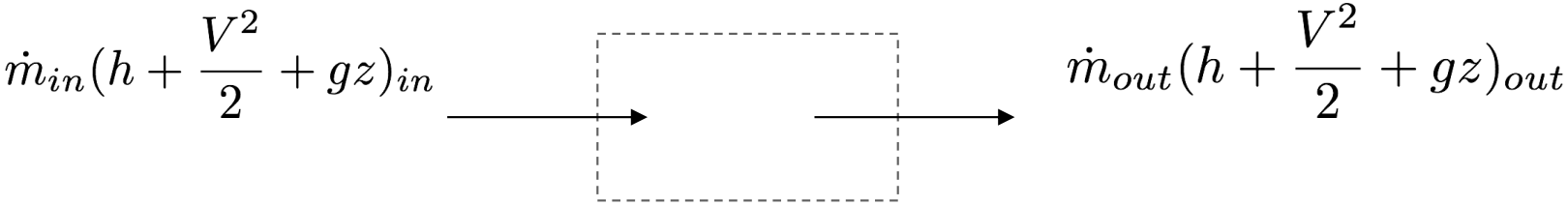
$$\dot{m}_{out}(h + \frac{V^2}{2} + gz)_{out} - \dot{m}_{in}(h + \frac{V^2}{2} + gz)_{in} = \dot{Q}_{in} - \dot{W}_{out}$$



Adiabatic Flame Temperature

- AFT - Temperature following reaction in absence of heat transfer or work

$$\dot{m}_{out}(h + \frac{V^2}{2} + gz)_{out} = \dot{m}_{in}(h + \frac{V^2}{2} + gz)_{in}$$



Heat of Combustion

- Heat of Combustion - Heat transfer achievable when products are cooled to reactant temperature

$$\dot{Q}_{out} = \dot{m}_{in}(h + \frac{V^2}{2} + gz)_{in} - \dot{m}_{out}(h + \frac{V^2}{2} + gz)_{out}$$

