Thermodynamics Review

- Equations of state
- Ideal gas mixtures
- Specific heats
- First Law of thermodynamics

Equations of state

- Relates P, V & T of a substance
- mass based

$$PV = mRT$$

- molar based

$$PV = NR_u T$$

$$R = \frac{R_u}{MW}$$

$$MW = \frac{m}{N}$$

Specific heats

- Constant volume and constant pressure specific hea

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$$

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_P .$$

- From caloritic equations of state, internal energy and enthalpy can be evaluated by

$$u(T) - u_{\text{ref}} = \int_{T_{\text{ref}}}^{T} c_v \, \mathrm{d}T$$

$$h(T) - h_{\text{ref}} = \int_{T_{\text{ref}}}^{T} c_p \, \mathrm{d}T .$$

- Specific heats depends on the energy storage modes available to a molecule
- Depending on the type of molecule, the energy storage modes are
    - Translational (kinetic)
    - Rotational
    - Vibrational
    - Electronic

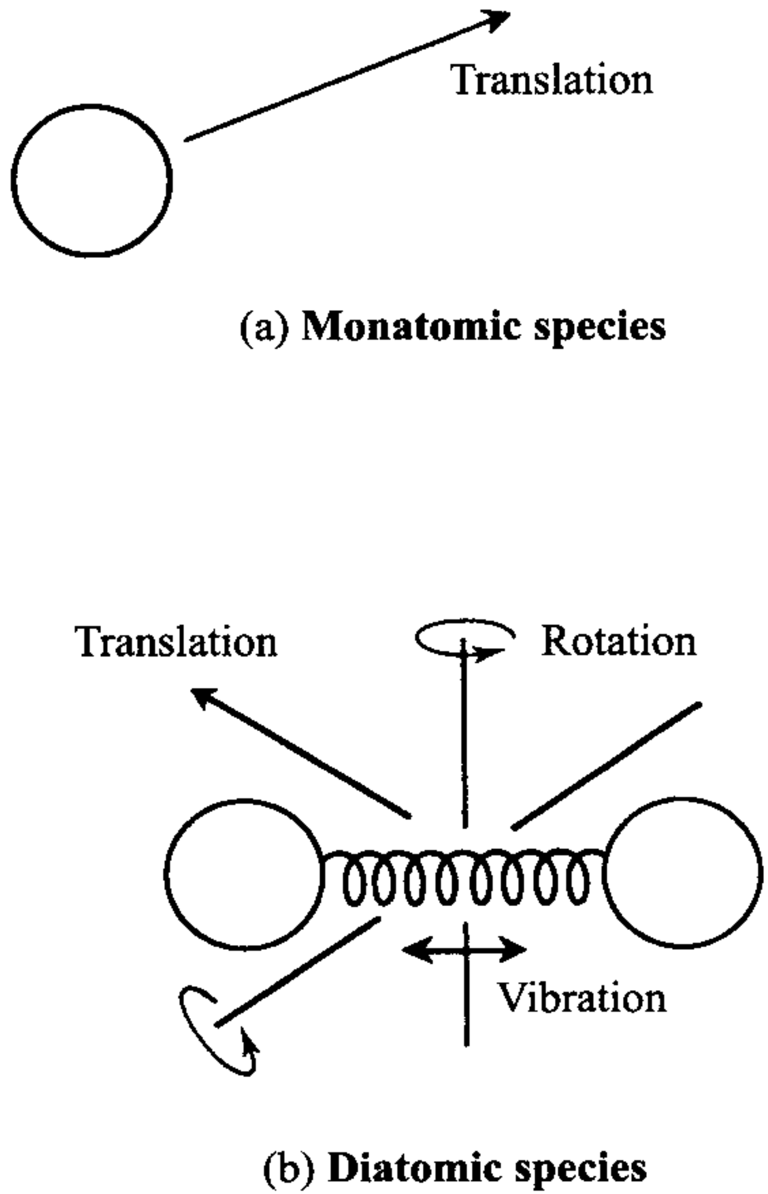

Figure 2.1 (a) The internal energy of monatomic species consists only of translational (kinetic) energy, while (b) a diatomic species' internal energy results from translation together with energy from vibration (potential and kinetic) and rotation (kinetic).

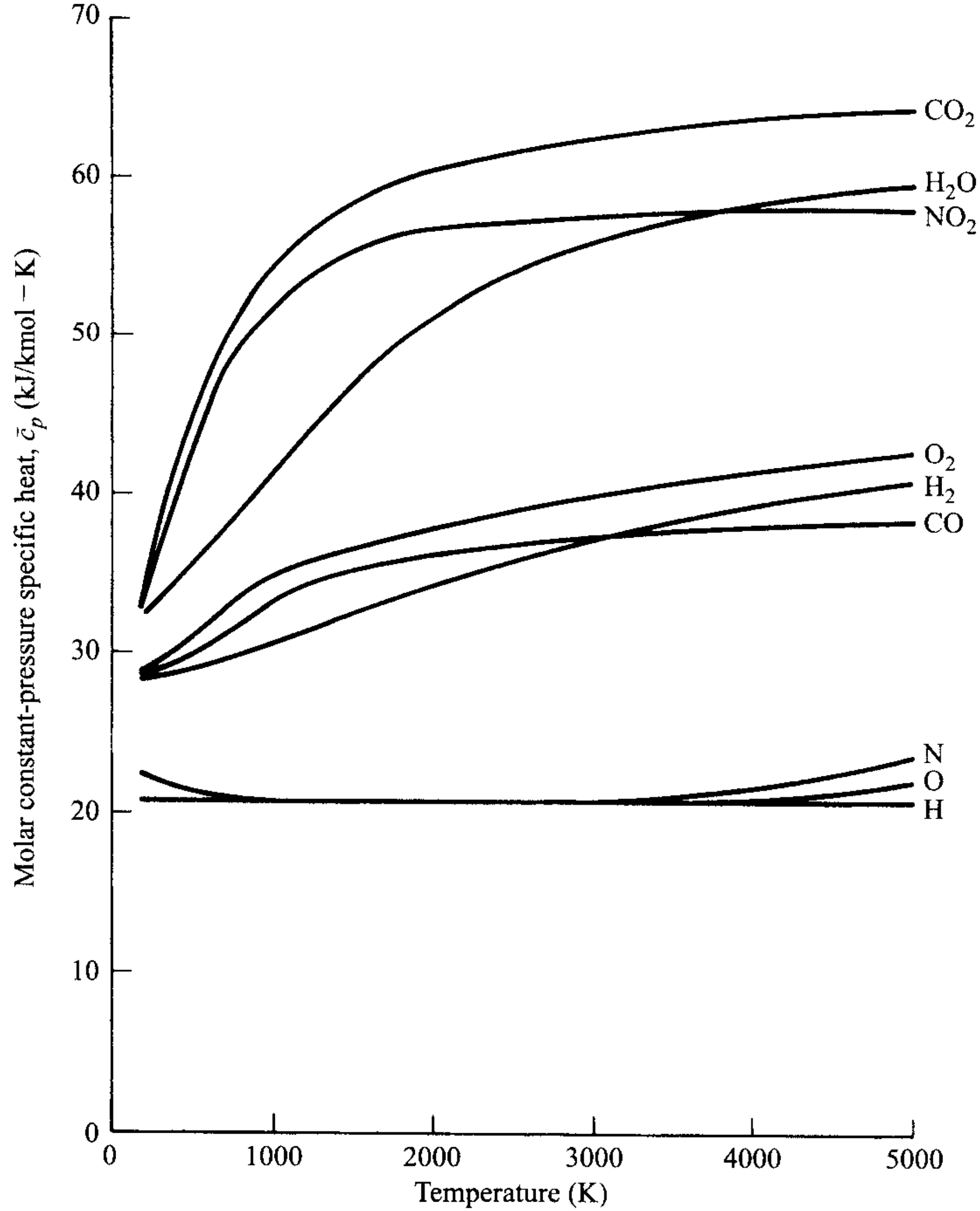

Figure 2.2 Molar constant-pressure specific heats as functions of temperature for monatomic (H, N, and O), diatomic (CO, H_2, and O_2), and triatomic (CO_2, H_2O, and NO_2) species. Values are from Appendix A.

NASA Polynomials

The equations below for nondimensional specific heat, enthalpy, and entropy, are given in Sanford and Bonnie (1994). Eqs. 4.6-4.8 are the "old" NASA format, and Eqs. 4.9-4.11 are the "new" NASA format as discussed in this file.

Eq. 4.6: $Cp0/R = a1 + a2*T + a3*T^2 + a4*T^3 + a5*T^4$

Eq. 4.7: $H0/RT = a1 + a2/2*T + a3/3*T^2 + a4/4*T^3 + a5/5*T^4 + a6/T$

Eq. 4.8: $S0/R = a1*\ln(T) + a2*T + a3/2*T^2 + a4/3*T^3 + a5/4*T^4 + a7$

Eq. 4.9: $Cp0/R = a1*T^{-2} + a2*T^{-1} + a3 + a4*T + a5*T^2 + a6*T^3 + a7*T^4$

Eq. 4.10: $H0/RT = -a1*T^{-2} + a2*T^{-1}*\ln(T) + a3 + a4*T/2 + a5*T^2/3 + a6*T^3/4 + a7*T^4/5 + b1/T$

Eq. 4.11: $S0/R = -a1*T^{-2}/2 - a2*T^{-1} + a3*\ln(T) + a4*T + a5*T^2/2 + a6*T^3/6 + a7*T^4/4 + b2$

Record explanation

Record	Constants	Format	Column
1	Species name or formula	A24	1 to 24
	Comments (data source)	A56	25-80
2	Number of T intervals	I2	2
	Optional identification code	A6	4-9
	Chemical formulas, symbols, and numbers	5(A2,F6.2)	11-50
	Zero for gas and nonzero for condensed phases	I1	52
	Molecular weight	F13.5	53-65
	Heat of formation at 298.15 K, J/mol	F13.5	66-80
3	Temperature range	2F10.3	2-21
	Number of coefficients for Cp0/R	I1	23
	T exponents in empirical equation for Cp0/R	8F5.1	24-63
	{H0(298.15)-H0(0)}, J/mol	F15.3	66-80
4	First five coefficients for Cp0/R	5D16.8	1-80
5	Last three coefficients for Cp0/R	3D16.8	1-48
	Integration constants b1 and b2	2D16.8	49-80

... Repeat 3, 4, and 5 for each interval

Example (Chlorine)

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Example A.1:

CL2 Chlorine gas. TPIS 1989, v1, pt2, p88.
2 tpis89 CL 2.00 0.00 0.00 0.00 0.00 0 70.90540 0.000
200.000 1000.000 7 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 9181.110
3.46281724D+04 -5.54712949D+02 6.20759103D+00 -2.98963673D-03 3.17303416D-06
-1.79363467D-09 4.26005863D-13 0.00000000D+00 1.53407075D+03 -9.43835303D+00
1000.000 6000.000 7 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0 0.0 9181.110
6.09256675D+06 -1.94962688D+04 2.85453491D+01 -1.44996828D-02 4.46388943D-06
-6.35852403D-10 3.32735931D-14 0.00000000D+00 1.21211722D+05 -1.69077832D+02
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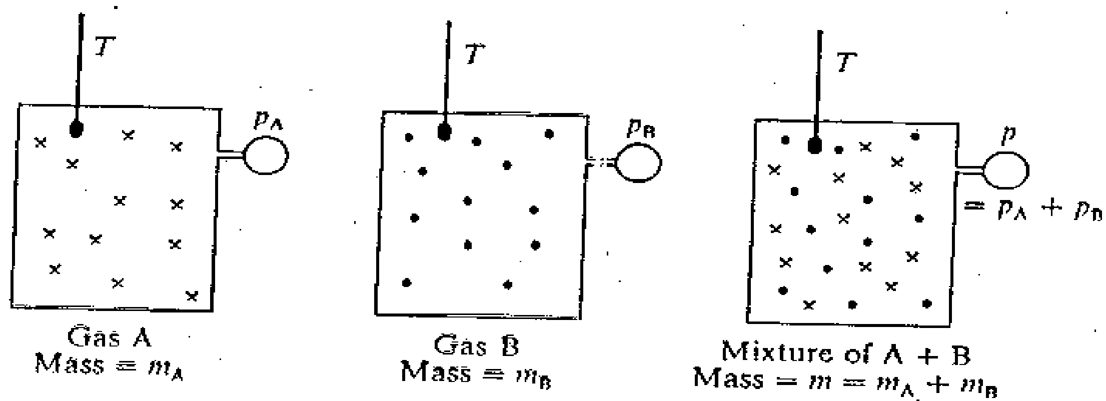
Mixtures

- Using Dalton's law

Mixtures

Fig. 6.1 Gas A mixing with gas B



- Partial pressure

$$P = \sum_i P_i.$$

Mixtures

- Mole fraction of species *i*

$$\chi_i \equiv \frac{N_i}{N_1 + N_2 + \ldots N_i + \ldots} = \frac{N_i}{N_{\text{tot}}}.$$

- Mass fraction of species *i*

$$Y_i \equiv \frac{m_i}{m_1 + m_2 + \ldots m_i + \ldots} = \frac{m_i}{m_{\text{tot}}}.$$

- The sum must be unity

$$\sum_i \chi_i = 1$$

$$\sum_i Y_i = 1.$$

- Can relate mole and mass fractions via molecular weight;

$$Y_i = \chi_i MW_i / MW_{\text{mix}}$$

$$\chi_i = Y_i MW_{\text{mix}} / MW_i.$$

- Average intensive properties of mixtures

$$MW_{\text{mix}} = \sum_i \chi_i MW_i$$

$$h_{\text{mix}} = \sum_i Y_i h_i \qquad s_{\text{mix}}(T, P) = \sum_i Y_i s_i(T, P_i)$$

$$\bar{h}_{\text{mix}} = \sum_i \chi_i \bar{h}_i. \qquad \bar{s}_{\text{mix}}(T, P) = \sum_i \chi_i \bar{s}_i(T, P_i).$$

First Law (Energy Balance)

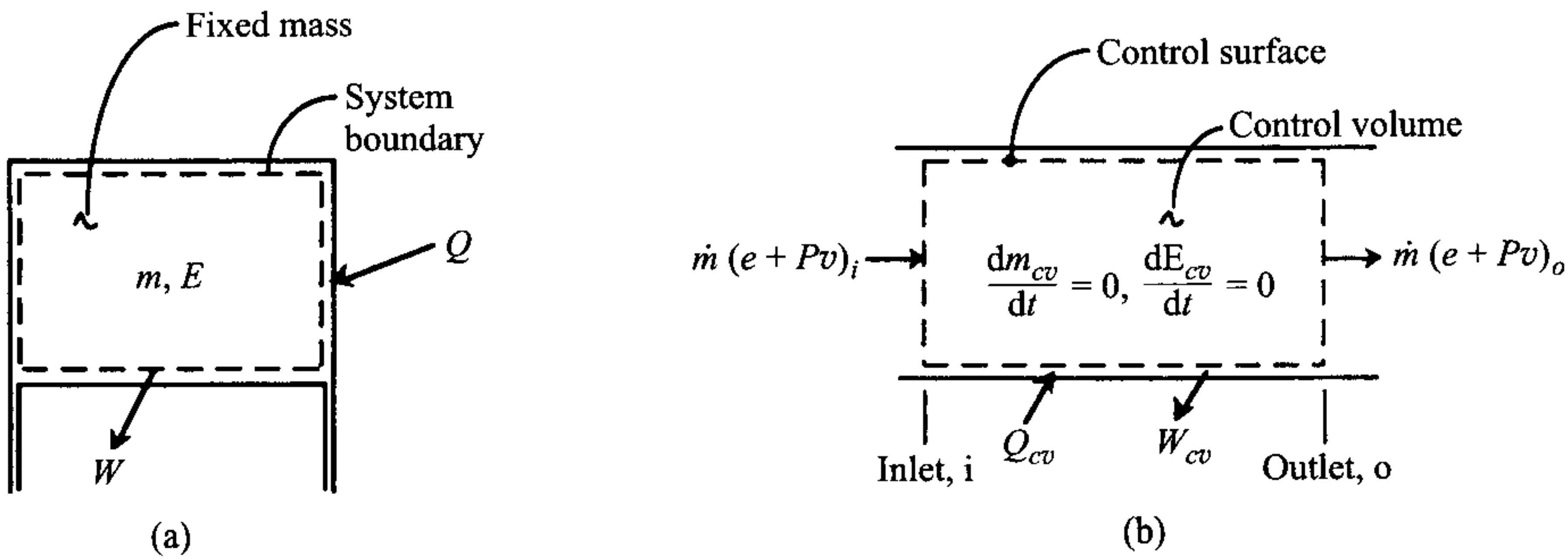


Figure 2.3 (a) Schematic of fixed-mass system with moving boundary above piston. (b) Control volume with fixed boundaries and steady flow.

1st Law

- Fixed mass (closed system)

$$ {}_1Q_2 \quad - \quad {}_1W_2 \quad = \quad \Delta E_{1-2} \qquad (2.20) $$

${}_1Q_2$	$-$	${}_1W_2$	$=$	ΔE_{1-2}
Head added to system in going from state 1 to state 2		Work done by system on surroundings in going from state 1 to state 2		Change in total system energy in going from state 1 to state 2

- Control volume (open system)

$$ \dot{Q}_{cv} - \dot{W}_{cv} = \dot{m}e_o - \dot{m}e_i + \dot{m}(P_o v_o - P_i v_i), $$

$\dot{Q}_{cv}$	$-$	$\dot{W}_{cv}$	$=$	$\dot{m}e_o$	$-$	$\dot{m}e_i$	$+$	$\dot{m}(P_o v_o - P_i v_i)$,
Rate of heat transferred across the control surface from the surroundings, to the control volume		Rate of all work done by the control volume, including shaft work, but excluding flow work		Rate of energy flowing out of the control volume		Rate of energy flowing into the control volume		Net rate of work associated with pressure forces where fluid crosses the control surface, flow work