Chapter 3 (conti.)

First Law of Thermodynamics and Energy Equation

The Constant-V and Constant-P specific heats

- ***Specific heat***
  - The amount of heat required <u>per unit mass</u> to raise the temperature by one degree. ($C = \delta q/dT$, unit: J/(kg K))
  - ***Constant-volume specific heat*** ***(thermodynamic property)***
    - From $\delta Q = dU + \delta W = dU + P\cancel{dV}$,

$$C_v = \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$$

  - ***Constant-pressure specific heat*** ***(thermodynamic property)***
    - From $\delta Q = dU + \delta W = dU + PdV = dU + d(PV) = dH$,

$$C_p = \frac{1}{m}\left(\frac{\partial Q}{\partial T}\right)_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p$$

- Specific heat in *solids and liquids*
  - Assuming that a solid or a liquid is nearly incompressible,

$$dh = du + d(Pv) \approx du + vdP$$

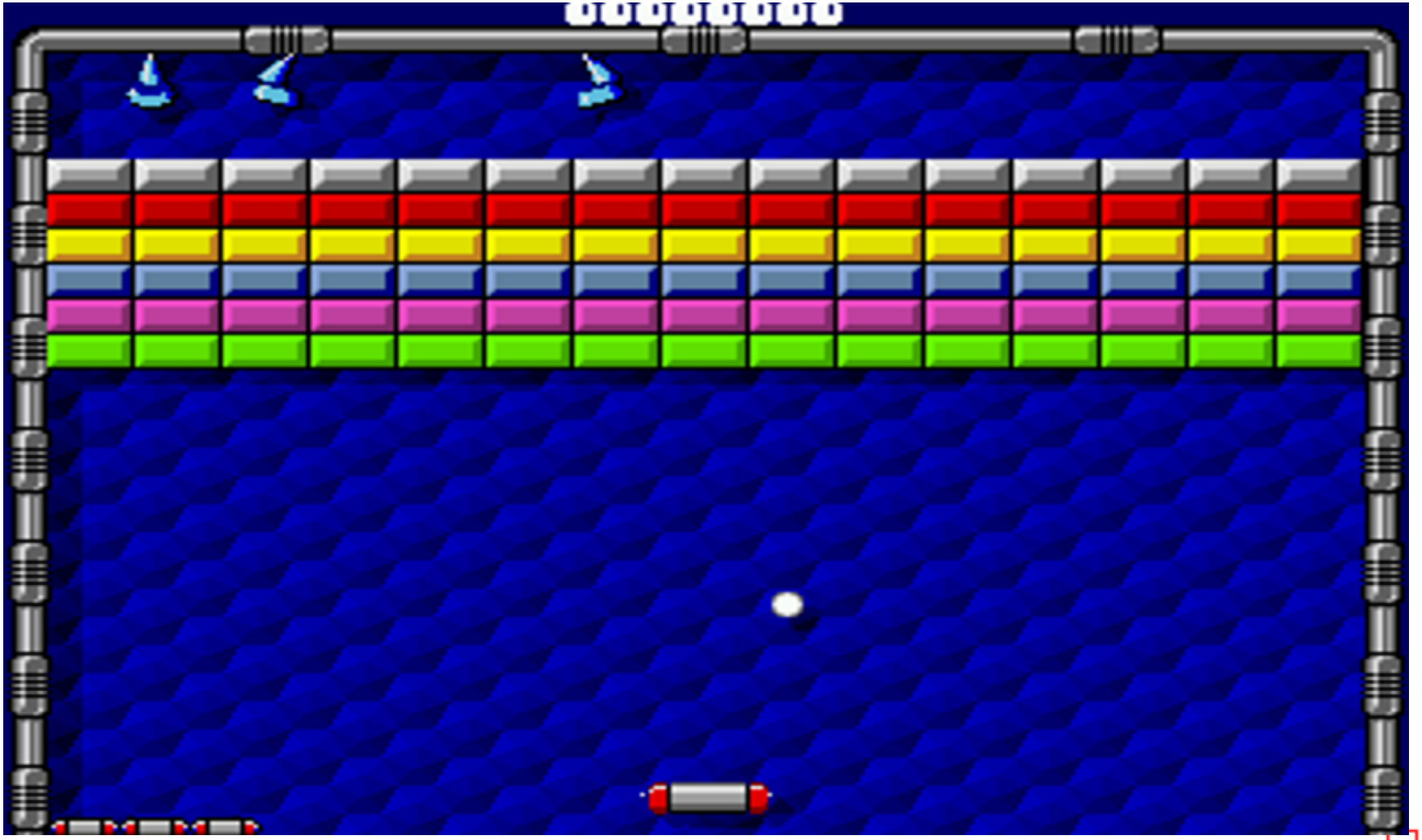
  - As the specific volume *v* is negligible in solids and liquids,

$$dh \approx du \approx CdT$$

  - In practice, we can consider *C* to be constant. Then,

$$h_2 - h_1 \simeq u_2 - u_1 \simeq C(T_2 - T_1)$$

(* Refer to Tables A.3 and A.4)



Special Case: Ideal Gases

- The internal energy of an ideal gas is ***a function of T only***.
- Then we can rewrite the constant-volume specific heat of an ideal gas:

$$\boxed{C_{v0} = \frac{du}{dT} \quad \text{or} \quad du = C_{v0}dT}$$

$$\Rightarrow C_{v0} = C_{v0}(T)$$
$$\Rightarrow dU = mC_{v0}dT$$

- The enthalpy of an ideal gas is also ***a function of T only***.
  - *h = u + Pv = u(T) + RT*
- Likewise, the enthalpy of an ideal gas becomes

$$\boxed{C_{p0} = \frac{dh}{dT} \quad \text{or} \quad dh = C_{p0}dT}$$

$$\Rightarrow C_{p0} = C_{p0}(T)$$
$$\Rightarrow dH = mC_{p0}dT$$

- C_{P0} and C_{v0} are also functions of temperature.
  - can be obtained from statistical thermodynamics. (appendix C)
  - change with temperature by contribution of molecular vibration to the specific heat.

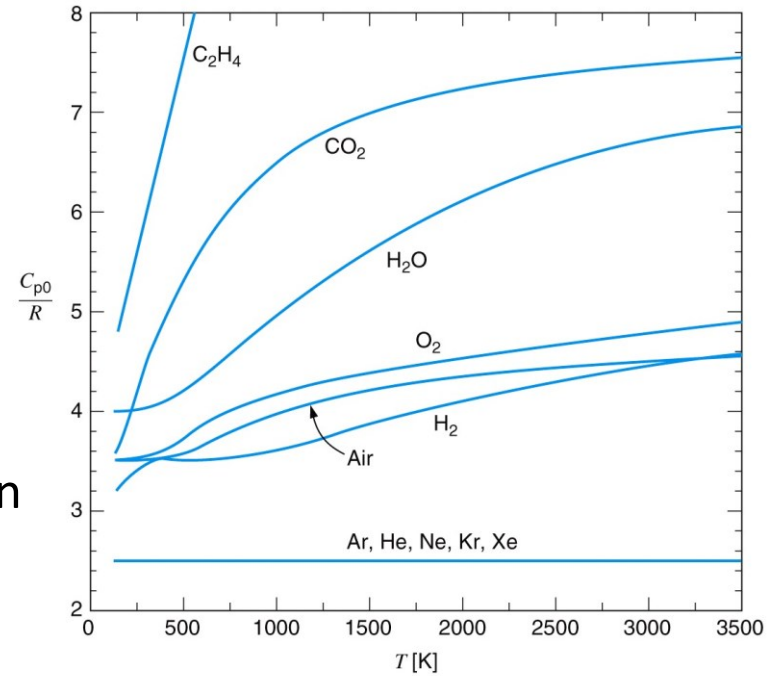


Figure 3.26
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- From the definition of enthalpy,

$$dh = du + d(Pv) = du + RdT \qquad \text{(ideal gas)}$$

$$C_{p0}dT = C_{v0}dT + RdT$$

$$\therefore C_{p0} = C_{v0} + R \qquad \text{or} \qquad \overline{C}_{p0} = \overline{C}_{v0} + \overline{R}$$

Integral Expression of Enthalpy (ideal gas)

$$\int_1^2 dh = h_2 - h_1 = \int_{T_1}^{T_2} C_{p0}(T)dT \quad \text{(ideal gas)}$$

When C_{p0} is constant,

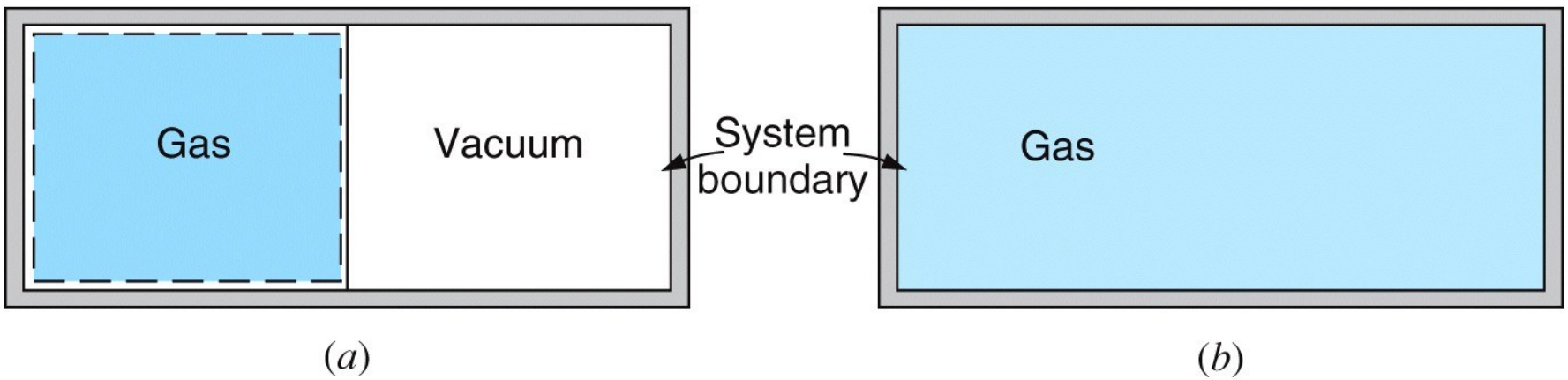
$$h_2 - h_1 = C_{p0}(T_2 - T_1)$$

When h is tabulated with respect to temperature,

$$h_2 - h_1 = \int_{T_0}^{T_2} C_{p0}(T)dT - \int_{T_0}^{T_1} C_{p0}(T)dT = h(T_2) - h(T_1)$$

(T_0 is a reference T, and the enthalpy at the reference T cancels out.)

Free Expansion



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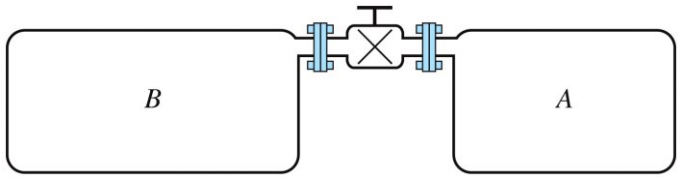
- Not a quasi-equilibrium process
- Expansion into the vacuum : $w = 0$
- No change in internal energy : $\Delta u = 0$
- Adiabatic process : $q = 0$

Rate Equations and Mass Conservation

- Rate of expansion work

$$\dot{W} = \frac{dW}{dt} = \frac{PdV}{dt} = P\dot{V}$$

- Mass conservation
  - Mixing after opening the valve



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$$m_2 = m_1 = m_{1A} + m_{1B}$$ (the continuity equation, mass conservation)

$$m_2 e_2 - (m_{1A} e_{1A} + m_{1B} e_{1B}) = {}_1Q_2 - {}_1W_2$$ (energy equation)

$$m_2 u_2 - (m_{1A} u_{1A} + m_{1B} u_{1B}) = {}_1Q_2 - {}_1W_2$$ (Negligible *ke* and *pe*)

$$\therefore \quad u_2 = \frac{m_{1A}}{m_2} u_{1A} + \frac{m_{1B}}{m_2} u_{1B} + \frac{{}_1Q_2 - {}_1W_2}{m_2}$$