III. Properties of Pure Substances

I. Specific Heats

1. We can't directly measure changes in internal energy, Δu, but we can measure changes in T and v. The change in u is proportional to the change in temperature, $\Delta u \propto \Delta T$.
   a. For a pure substance, it is convenient to let u = f(T,v)
   b. Then in a closed system at <u>constant volume</u>,

$$du = c_v dT \;\; or \;\; \Delta U = m\int_{T_1}^{T_2} c_v(T)dT \;\; or \;\; \Delta U = mc_{v,ave}(T_2 - T_1)$$

   c. Define specific heat at constant volume as

(4-19) $$c_v = \left(\frac{\partial u}{\partial T}\right)_v \quad \left(\frac{kJ}{kg \cdot K}\right)$$

Temperature unit is temperature difference.

   d. In words: c_v is the thermal energy required to raise the temperature of 1 kg by 1 degree K or C at constant volume.

III. Properties of Pure Substances

2. We can't directly measure changes in enthalpy, Δh, but we can measure changes T and p. The change in h is proportional to the change in temperature, $\Delta h \propto \Delta T$.
   a. For a pure substance, it is convenient to let $h = f(T,p)$
   b. Then in a closed system at <u>constant pressure</u>,

$$dh = c_p dT \;\; or \;\; \Delta H = m\int_{T_1}^{T_2} c_p(T)dT \;\; or \;\; \Delta H = mc_{p,ave}(T_2 - T_1)$$

   c. Define specific heat at constant pressure as

(4-20) $$c_p = \left(\frac{\partial h}{\partial T}\right)_p \quad \left(\frac{kJ}{kg \cdot K}\right)$$

Temperature is temperature difference.

   d. In words: c_p is the thermal energy required to raise the temperature of 1 kg by 1 degree K or C at constant pressure.

III. Properties of Pure Substances

e. Why do we have two heat capacities?

Constant Pressure Processes

The amount of electrical energy required to heat 1 kg of air flowing through a blow dryer from T_1 to T_2 is given by

$$Q_{in,elec} = \Delta h = c_P(T_2 - T_1)$$

$$c_{p,air} = 1.005\ kJ/(kg\ K)$$

Constant Volume Processes

The amount of chemical energy required to heat 1 kg of the gases in an internal combustion engine, at the start of the power stroke, from T_1 to T_2 is approximated by

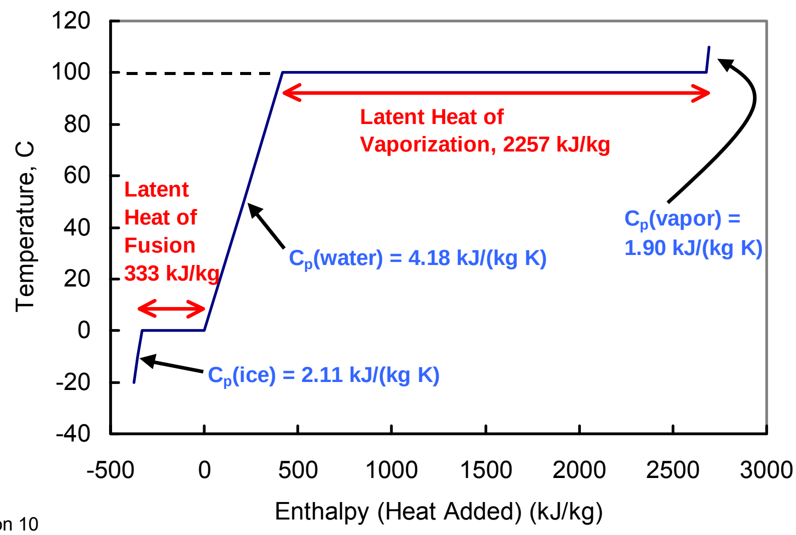
$$Q_{in,chem} = \Delta u = c_V(T_2 - T_1)$$

$$c_{v,air} = 0.718\ kJ/(kg\ K)$$

$c_p > c_v$ because in a constant pressure process the hot gases can expand as they are heated which means that work will be performed by the gases on the surroundings. Hence, more heat must be added in a constant pressure process to achieve the same temperature rise.

III. Properties of Pure Substances

f. Example: c_p for water at constant pressure of 1 atm.



III. Properties of Pure Substances

3. Internal Energy, Enthalpy, and Specific Heat Relationships for Ideal Gases

   a. Internal energy is a function only of T (for ideal gases)

$$u = u(T) \text{ and } du = c_v(T)dT \qquad \boxed{\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c_v(T)dT} \qquad (4\text{-}25)$$

   b. Enthalpy is a function only of T (for ideal gases)

$$h = h(T) \text{ and } dh = c_p(T)dT \qquad \boxed{\Delta h = h_2 - h_1 = \int_{T_1}^{T_2} c_p(T)dT} \qquad (4\text{-}26)$$

lesson 10

III. Properties of Pure Substances

3. Internal Energy, Enthalpy, and Specific Heat Relationships for Ideal Gases

   c. Relationship between c_p and c_v (for ideal gases)

$$h = u + pv = u + RT$$
$$dh = du + RdT \qquad \boxed{c_p - c_v = R \quad (\text{ideal gas})} \qquad (4\text{-}29)$$
$$c_p dT = c_v dT + RdT$$

   d. c_p and c_v depend only on T (for ideal gases)

lesson 10

III. Properties of Pure Substances

4. Example - Is the heat rejected by my old truck directly contributing to global warming?
   a. System is atmosphere of earth. m_{atm} = 5.14x10^{18} kg
   b. Heat capacity of air at 300 K is c_p = 1.005 kJ/(kg K)
   c. Heating value of world's petroleum reserves is ΔH_{pet} = 10^{19} kJ
   d. An energy balance assuming world's entire petroleum reserves are burned instantly and heat is distributed over entire mass of atmosphere

$$Q = \Delta U + P\Delta V = \Delta H_{pet} = m_{atm} c_p \Delta T$$

III. Properties of Pure Substances

4. Example - Is the heat rejected by my old truck directly contributing to global warming?

$$\Delta T = \frac{\Delta H_{pet}}{c_p m_{atm}} = \frac{10^{19}\ kJ}{1.005 \frac{kJ}{kg \cdot K} 5.14x10^{18}\ kg} = 2\ K = 2\ C$$

   e. Conclusions. The direct effect of old truck on temperature of atmosphere is negligible . We must consider, however, indirect effects. The rate at which solar energy is absorbed by the earth is 3.8x10^{24} J/y. Anything which acts to increase retention of this energy in the atmosphere could cause large increases in global temperature.

III. Properties of Pure Substances

5. Evaluation of integrals of $c_v dT$ and $c_p dT$ for ideal gases - in order of decreasing accuracy

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c_v dT \qquad \Delta h = h_2 - h_1 = \int_{T_1}^{T_2} c_p dT$$

a. Use equation such as $c_p = a + bT + cT^2 + dT^3$ that is based on experimental data (Table A-2c).

b. Use tabulated data (Tables A-2a,b). This may involve interpolation.

c. Use an arithmetically averaged temperature to evaluate c.

d. Use the value of c at the initial temperature and assume constant.

III. Properties of Pure Substances

6. Properties of incompressible substances

a. Density and specific volume of liquids and solids are approximately constant: v = constant or ρ = constant

b. Internal energy of incompressible substances is a function only of T

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = c_v dT \qquad \text{(incompressible)}$$

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c(T)dT \qquad \text{(incompressible)} \qquad (4\text{-}34)$$

$$or \quad \Delta U = mc_{v,ave}(T_2 - T_1) \qquad \text{(incompressible)} \qquad (4\text{-}35)$$

III. Properties of Pure Substances

c. Enthalpy of an incompressible substance is a function of T and P

$$h = u + pv$$
$$h_2 - h_1 = u_2 - u_1 + v(p_2 - p_1)$$

(incompressible)

$$\Delta h = h_2 - h_1 = \int_{T_1}^{T_2} c\,dT + v(p_2 - p_1)$$

(incompressible)

d. For an incompressible substance, $c_p = c_v = c$

e. Variation of c with T is small for solids and liquids.
Evaluate c at average T: $\Delta h = \Delta u + v\Delta p = c_{av}\Delta T + v\,\Delta p$. (4-37)

lesson 10