

Chapter 5 Energy Equation for a Control Mass

the first law of thermodynamics \longleftrightarrow the conservation of energy law

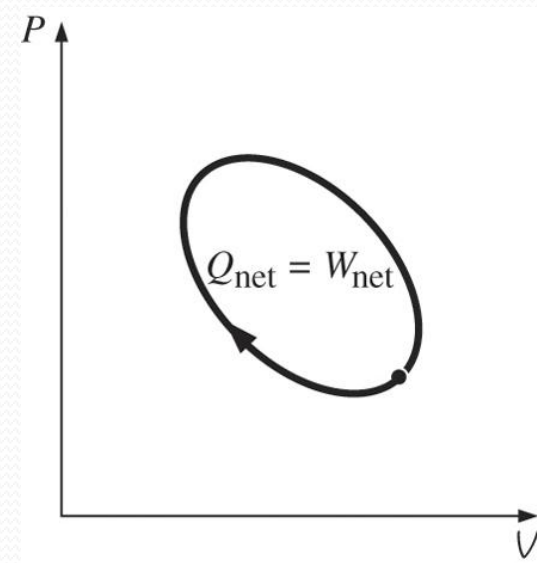
For a Cycle of a Control Mass

The first law of thermodynamics states that during any cycle a system (control mass) undergoes, the cyclic integral of the heat is proportional to the cyclic integral of the work.

A system is said to have undergone a cycle if it returns to its initial state at the end of the process.

The initial and final states are identical for a cycle so there is no difference for point function properties.

$$\Delta E = E_{final} - E_{initial} = \Delta U + \Delta KE + \Delta PE = 0$$



For a cycle $\Delta E = 0$, thus $Q = W$.

$$W_{\text{net,out}} = Q_{\text{net,in}} \quad \text{or} \quad \dot{W}_{\text{net,out}} = \dot{Q}_{\text{net,in}} \quad \text{Energy balance for a cycle}$$

where

$$Q = Q_{\text{net,in}} = Q_{\text{in}} - Q_{\text{out}}$$

and

$$W = W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$$

For a Change In State of a Control Mass

Considering the two separate processes

$$\oint \delta Q = \oint \delta W$$

i) Process A and Process B

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B$$

ii) Process C and Process B

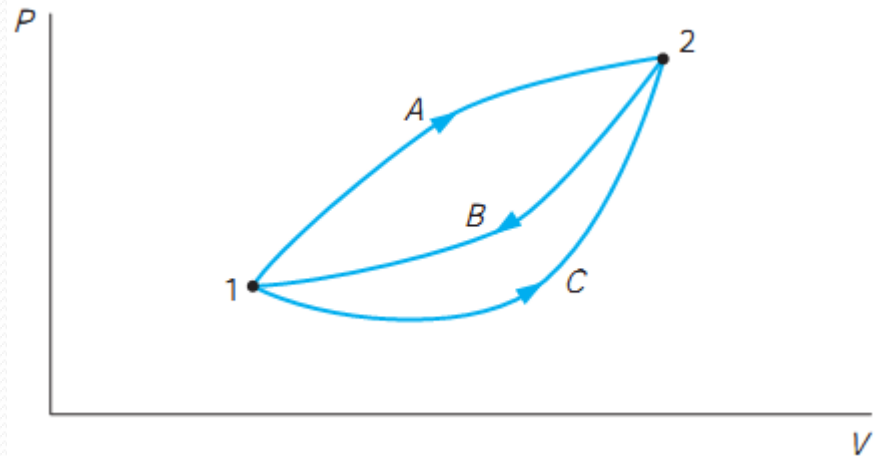
$$\int_1^2 \delta Q_C + \int_2^1 \delta Q_B = \int_1^2 \delta W_C + \int_2^1 \delta W_B$$

Subtracting the second of these equations from the first, we obtain

$$\int_1^2 \delta Q_A - \int_1^2 \delta Q_C = \int_1^2 \delta W_A - \int_1^2 \delta W_C$$

or, by rearranging,

$$\int_1^2 (\delta Q - \delta W)_A = \int_1^2 (\delta Q - \delta W)_C$$



Since A and C represent arbitrary processes between states 1 and 2, the quantity $\delta Q - \delta W$ is the same for all processes between states 1 and 2. Therefore, $\delta Q - \delta W$ depends only on the initial and final states and not on the path followed between the two states. We conclude that this is a point function, and therefore it is the differential of a property of the mass.

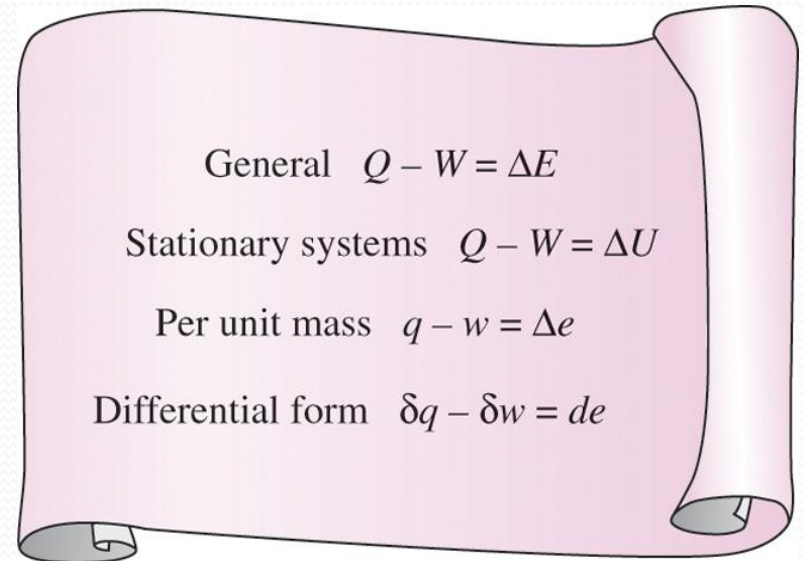
This property is the **energy** of the mass and is given the symbol E . Thus we can write

$$dE = \delta Q - \delta W$$

Because E is a property, its derivative is written dE . When above equation is integrated from an initial state 1 to a final state 2, we have

$$E_2 - E_1 = {}_1Q_2 - {}_1W_2$$

where E_1 and E_2 are the initial and final values of the energy E of the control mass, ${}_1Q_2$ is the heat transferred to the control mass during the process from state 1 to state 2, and ${}_1W_2$ is the work done by the control mass during the process.



Various forms of the first-law relation for closed systems when sign convention is used. (For a stationary system $\Delta KE = \Delta PE = 0$)

The first law of thermodynamics for a change of state may therefore be written

$$dE = dU + d(KE) + d(PE) = \delta Q - \delta W$$

$$dE = dU + d(KE) + d(PE)$$

where dKE and dPE are

$$dKE = F dx = mV dV \qquad F = ma = m \frac{dV}{dt} = m \frac{dx}{dt} \frac{dV}{dx} = mV \frac{dV}{dx}$$

$$dPE = F dZ = m g dZ \qquad F = ma = m g$$

Substituting the expressions for kinetic and potential energy into first equation

$$dE = dU + mV dV + m g dZ$$

Integrating for a change of state from state 1 to state 2 with constant g

$$E_2 - E_1 = U_2 - U_1 + \frac{mV_2^2}{2} - \frac{mV_1^2}{2} + m g Z_2 - m g Z_1$$

$$dE = dU + \frac{d(mV^2)}{2} + d(m g Z) = \delta Q - \delta W$$



Internal Energy: A Thermodynamic Property

Internal energy is an extensive property because it depends on the mass of the system. Similarly, kinetic and potential energies are extensive properties.

U internal energy

extensive property

**u the internal energy per unit mass
or the specific internal energy**

intensive property

However, because the context will usually make it clear whether u or U is referred to, we will simply use the term internal energy to refer to both internal energy per unit mass and the total internal energy.



Values for internal energy are found in the steam tables in the same manner as for specific volume.

In the liquid-vapor saturation region,

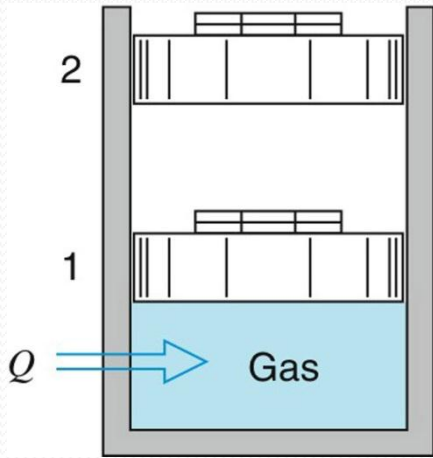
$$U = U_{liq} + U_{vap} \quad \text{or} \quad mu = m_{liq} u_f + m_{vap} u_g$$

Dividing by m and introducing the quality of x gives

$$u = (1 - x)u_f + xu_g \quad \text{or} \quad u = u_f + xu_{fg} \quad \text{Same form with specific volume}$$

The Thermodynamic Property Enthalpy

Enthalpy H is the sum of the internal energy U and the pressure-volume product PV .



Consider a control mass undergoing a quasi-equilibrium **constant-pressure** process

Assume that Kinetic and potential energy $\Delta KE = 0$, $\Delta PE = 0$

Only work done during the process is that associated with the boundary movement.

$${}_1W_2 = P \int_1^2 dV = P(V_2 - V_1)$$

Taking the gas as our control mass and applying the first law

$${}_1Q_2 - {}_1W_2 = U_2 - U_1$$

The heat transfer during the process is given in terms of the change in the quantity $U + PV$ between the initial and final states.

All these quantities are thermodynamic properties and functions only of the state of the system, their combination ($H = U + PV$) must also have these same characteristics.

the **enthalpy**,

$$H = U + PV$$

or, per unit mass, $h = u + Pv$

$$h = h_f + x h_{fg}$$

Some tables and charts of thermodynamic properties give values for enthalpy but not for the internal energy. Therefore, it is necessary to calculate the internal energy at a state using the tabulated enthalpy values and rearranging form of above equation

$$u = h - Pv$$



Problem Analysis and Solution Technique

Our problem analysis and solution technique is contained within the framework of the following set of questions

- i) It may be helpful to draw a sketch of the system, illustrating all heat and work flows, and indicating forces such as external pressures and gravitation. (**determination of energy transfer mechanism and forces**)
- ii) What do we know about the initial state and the final state? (i.e., which properties are known)? (**determination of states**)
- iii) What do we know about the process that takes place? Is anything constant or zero? Is there some known functional relation between two properties? (**determination of boundary work process and state properties by using state relations**)



iv) Is it helpful to draw a diagram of the information (for example, a T - v or P - v diagram)? (**may show the process and states**)

v) What is our thermodynamic model for the behavior of the substance (for example, steam tables, ideal gas, and so on)? (**the methods to drive thermodynamic properties**)

vi) What is our analysis of the problem (i.e., do we examine control surfaces for various work modes or use the first law or conservation of mass)? (**determination of properties from the relation between them**)

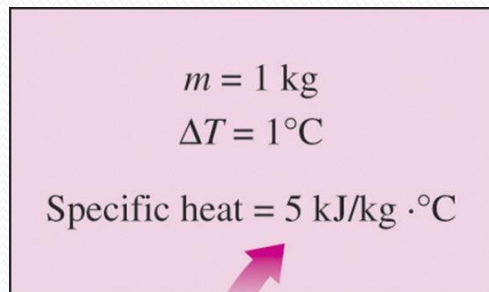
vii) what we have done so far in previous steps, how do we proceed to find whatever it is that is desired? Is a trial-and-error solution necessary? (**another methods such as trial and error**)

The Constant–Volume and Constant–Pressure Specific Heats

Consider a homogeneous phase of a substance of constant composition. It may be a solid, a liquid, or a gas, but no change of phase will occur.

Specific heat at constant volume, c_v : The energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant.

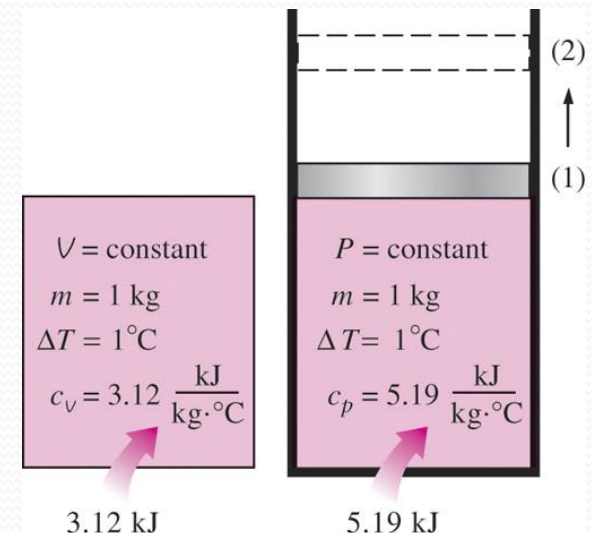
Specific heat at constant pressure, c_p : The energy required to raise the temperature of the unit mass of a substance by one degree as the pressure is maintained constant.



5 kJ

Constant-volume
and constant-
pressure specific
heats c_v and c_p
(values are for
helium gas).

Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way.



3.12 kJ

5.19 kJ

Constant volume, for which the work term ($P dV$) is zero, so that the specific heat (at constant volume) is

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

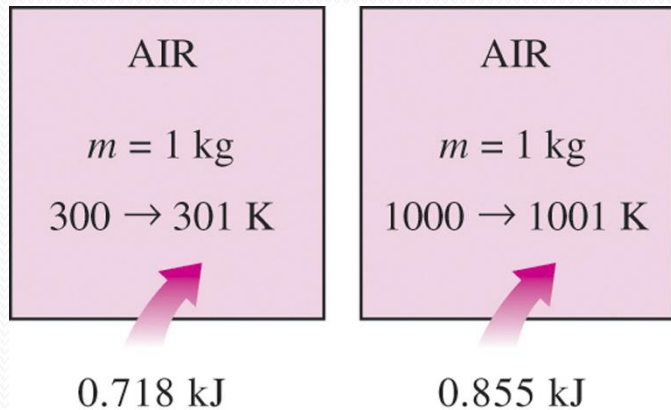
Constant pressure, for which the work term can be integrated and the resulting PV terms at the initial and final states can be associated with the internal energy terms, so that the specific heat (at constant pressure) is

$$C_P = \frac{1}{m} \left(\frac{\delta Q}{dT} \right)_P = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial h}{\partial T} \right)_P$$

c_v is related to the changes in *internal energy* and c_p to the changes in *enthalpy*.

A common unit for specific heats is $\text{kJ/kg} \cdot ^\circ\text{C}$ or $\text{kJ/kg} \cdot \text{K}$. **Are these units identical?**

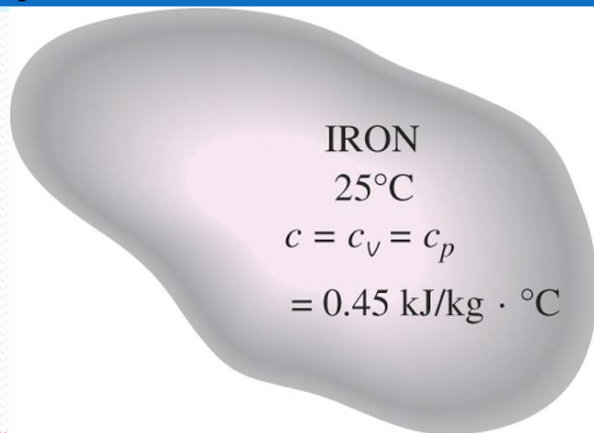




The specific heat of a substance changes with temperature.

True or False?

c_p is always greater than c_v .



Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids

Consider either a solid or a liquid, both of these phases are **nearly incompressible** (so $dv \approx 0$)

$$dh = du + v dP + P dv = du + v dP$$

Also, for both of these phases, **the specific volume is very small** ($vdp \approx 0$ for small volume and $dp=0$ for constant pressure process), such that in many cases

$$dh \approx du \approx C dT$$

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

C is either the constant -volume or the constant-pressure specific heat, as the two would be nearly the same.

$$C_P = C_V = C \quad \left(\frac{kJ}{kg \cdot K} \right)$$

For liquids, two special cases are commonly encountered

Since liquids are nearly incompressible

$$dh = du + v dP + P/dv = du + v dP$$

1. *Constant-pressure processes*, as in heaters ($\Delta P = 0$): $\Delta h = \Delta u \cong c_{\text{avg}} \Delta T$

2. *Constant-temperature processes*, as in pumps ($\Delta T = 0$): $\Delta h = v \Delta P$

Internal energy is dependent on temperature,
so $du=0$ for isothermal process

The enthalpy of a compressed liquid

$$h_{@P,T} \cong h_{f@T} + v_{f@T}(P - P_{\text{sat}@T})$$

A more accurate relation than

$$h_{@P,T} \cong h_{f@T}$$



Internal Energy, Enthalpy, and Specific Heats of Ideal Gases

In general, for any substance the internal energy u depends on the two independent properties specifying the state. For a low-density gas, however, u depends primarily on T and much less on the second property, P or v .

Internal Energy values for superheated vapor steam from Table 2.5.3

P, kPa				
T, °C	10	100	500	1000
200	2661.3	2658.1	2642.9	2621.9
700	3479.6	3479.2	3477.5	3475.4
1200	4467.9	4467.7	4466.8	4465.6

From these values, it is evident that u depends strongly on T , but not much on P . Also, we note that the dependence of u on P is less at low pressure and much less at high temperature

Dependence of u on P decreases $P \downarrow$ and $T \uparrow$ so the density ($\rho = P/(RT)$) decreases with dependence of u on P (or v)

Therefore reasonable to assume that as gas density becomes so low that the ideal-gas model is appropriate, internal energy does not depend on pressure at all but is a function only of temperature.

For an ideal gas, $Pv = RT$ and $u = f(T)$ only

Because the internal energy of an ideal gas is not a function of specific volume, for an ideal gas we can write

$$C_{vo} = \frac{du}{dT} \text{ instead of } C_v = \left(\frac{\partial u}{\partial T} \right)_v \longrightarrow du = C_{vo} dT \text{ and } dU = m C_{vo} dT$$

the subscript o denotes the specific heat of an ideal gas



From the definition of enthalpy and the equation of state of an ideal gas, we have

$$h = u + Pv = u + RT$$

Since R is a constant and u is a function of temperature only, the enthalpy, h , of an ideal gas is also a function of temperature only.

$$C_{P_o} = \frac{dh}{dT} \text{ instead of } C_P = \left(\frac{\partial h}{\partial T} \right)_P \longrightarrow dh = C_{P_o} dT \text{ and } dH = m C_{P_o} dT$$

Because the internal energy and enthalpy of an ideal gas are functions of temperature only, it also follows that the constant-volume and constant-pressure specific heats are also functions of temperature only.

$$C_{v_o} = f(T)$$

$$C_{P_o} = f(T)$$

$$\begin{aligned} u &= u(T) \\ h &= h(T) \\ c_v &= c_v(T) \\ c_p &= c_p(T) \end{aligned}$$

For ideal gases, u , h , c_v , and c_p vary with temperature only.



Three ways of calculating Δu and Δh of ideal gases

1. By using the tabulated u and h data. This is the easiest and **most accurate** way when tables are readily available.
2. By using the c_v or c_p relations (Öztürk's Table 2.4.1) as a function of temperature and performing the integrations. This is very inconvenient for hand calculations but quite desirable for computerized calculations. The results obtained are **very accurate**.
3. By using average specific heats. This is very simple and certainly very convenient when property tables are not available. The results obtained are **reasonably accurate** if the temperature interval is not very large.

$$\Delta u = u_2 - u_1 \text{ (table)}$$

$$\Delta h = h_2 - h_1 \text{ (table)}$$

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T) dT$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T) dT$$

$$\Delta u \cong c_{v,\text{avg}}(T_2 - T_1)$$

$$\Delta h \cong c_{p,\text{avg}}(T_2 - T_1)$$

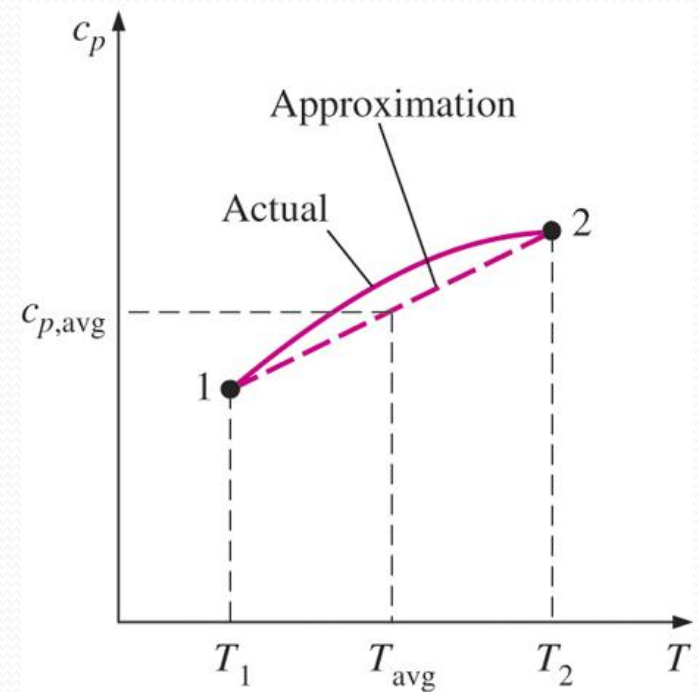
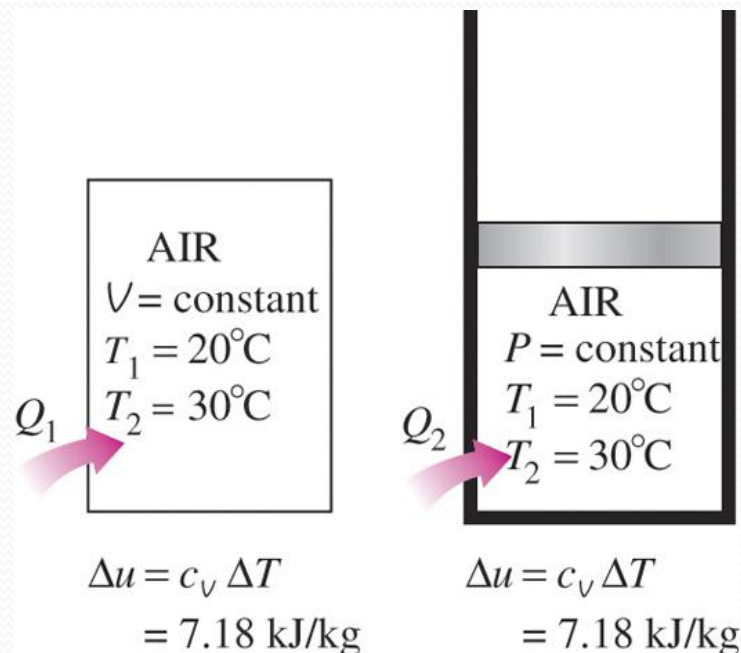
Three ways of
calculating Δu and Δh .

Specific heats for various solids and liquids are listed in Tables 2.2, 2.4.2, 3.2.*, 3.3.1, 3.4.*, and 3.5 from Öztürk's book.

Internal energy and enthalpy change when specific heat is taken constant at an average value

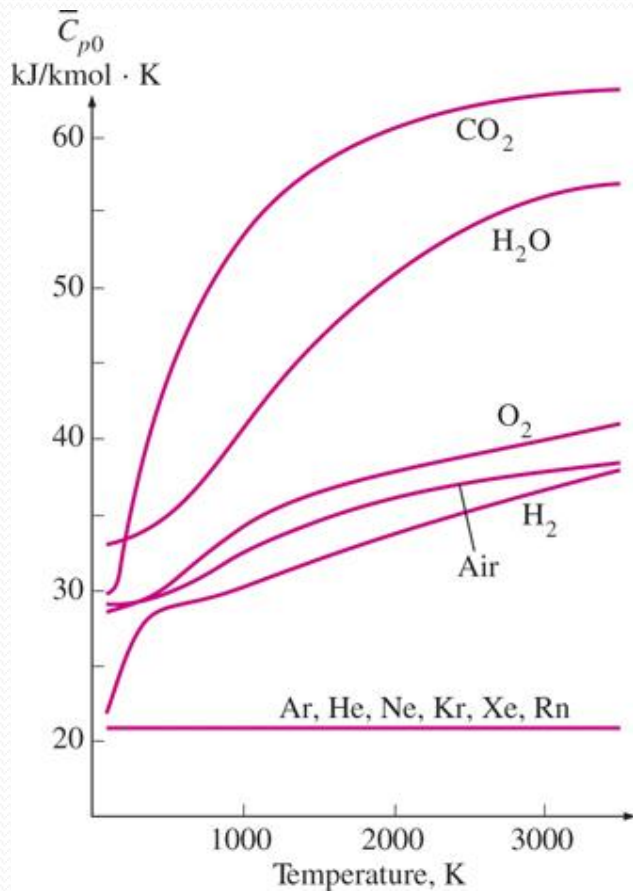
$$u_2 - u_1 = c_{v,\text{avg}}(T_2 - T_1) \quad (\text{kJ/kg})$$

$$h_2 - h_1 = c_{p,\text{avg}}(T_2 - T_1)$$



For small temperature intervals, the specific heats may be assumed to vary linearly with temperature.

The relation $\Delta u = c_v \Delta T$ is valid for *any ideal gas undergoing any process, constant-volume or not.*



Some observations can be made from Figure. First, the specific heats of gases with complex molecules (molecules with two or more atoms) are higher and increase with temperature.

Ideal-gas constant-pressure specific heats for some gases (see Table 2.4.1 for c_p equations).

Specific Heat Relations of Ideal Gases

$$\left. \begin{aligned} h &= u + Pv = u + RT \\ dh &= du + R dT \\ C_{Po} dT &= C_{vo} dT + R dT \end{aligned} \right\}$$

The relationship between c_p , c_v and R

$$C_{Po} - C_{vo} = R$$

On a molar basis

$$\bar{C}_{Po} - \bar{C}_{vo} = \bar{R}$$

$$k = \frac{C_{po}}{C_{vo}} \quad \text{Specific heat ratio}$$

The c_p of an ideal gas can be determined from a knowledge of c_v and R .

AIR at 300 K

$$\left. \begin{aligned} c_v &= 0.718 \text{ kJ/kg} \cdot \text{K} \\ R &= 0.287 \text{ kJ/kg} \cdot \text{K} \end{aligned} \right\} c_p = 1.005 \text{ kJ/kg} \cdot \text{K}$$

or

$$\left. \begin{aligned} \bar{c}_v &= 20.80 \text{ kJ/kmol} \cdot \text{K} \\ R_u &= 8.314 \text{ kJ/kmol} \cdot \text{K} \end{aligned} \right\} \bar{c}_p = 29.114 \text{ kJ/kmol} \cdot \text{K}$$

Conservation of Mass

A control mass is defined as a fixed quantity of mass. The question now is whether **the mass of such a system changes when its energy changes**.

$$E = mc^2$$

where c = velocity of light and E = energy.

For a rigid vessel that contains a 1-kg stoichiometric mixture of a hydrocarbon fuel (such as gasoline) and air, 2900 kJ energy transfer from the system after combustion. The velocity of light, c , is 2.9979×10^8 m/s

$$2900000 = m(2.9979 \times 10^8)^2 \longrightarrow m = 3.23 \times 10^{-11} \text{ kg}$$

We will not introduce significant error into most thermodynamic problems and our definition of a control mass as having a fixed mass can be used even though the energy changes.