

## Specific Heat

Measurement of heat interactions under closely controlled conditions have given much information on system properties during the development of thermodynamics. Such a measurement, related to a system of a pure substance of known mass, gives rise to a term called specific heat.

### specific heat at constant volume (C<sub>v</sub>)

Suppose we have as a system a quantity of pure gas such as nitrogen. This can undergo a process between equilibrium end states, and the first law equation applies as follows.

First law equation

$$Q - W = E_2 - E_1$$

Since we are considering a gas of certain mass at rest,

$$Q - W = U_2 - U_1$$

(16)

$$\text{or } \frac{Q - W}{m} = u_2 - u_1$$

At constant volume,  $W = 0$ .

$$\text{Hence, } \frac{Q}{m} = u_2 - u_1$$

The heat interaction  $Q/m$  is measured for constant volume conditions over very small temperature ranges to give in the limit the differential change in  $u$  with  $T$ , or

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

where  $c_v$  is the specific heat at constant volume ( $\text{kJ/kg K}$ ) or ( $\text{J/kg K}$ ).

The word, 'specific' is used since specific heat is the heat transfer necessary to change 1 kg of substance through 1 degree rise of temperature, in this case under constant volume conditions so that work effects are excluded.

As specific internal energy is an intensive property, the specific heat at constant volume must also be intensive.

Since 'u' depends only on end states and not on any path,  $\Delta u$  depends only on  $\Delta T$  and  $C_v$ . Between the same two end states we might have a constant volume process (used to measure the specific heat), or we might have any number of processes involving both heat and work. The change of internal energy will be the same.

### Specific heat at constant pressure ( $C_p$ )

Another special condition under which a heat interaction could be measured is at constant pressure. The First Law equation for the process becomes:

$$Q - W = U_2 - U_1$$

$$\text{or } Q - P(H_2 - H_1) = U_2 - U_1$$

$$\text{or } Q = (U_2 + PH_2) - (U_1 + PH_1)$$

$$\text{or } Q = H_2 - H_1 \quad \text{where } H = U + PV$$

$$\text{or } Q = m (h_2 - h_1)$$

$$\text{where } h = u + PV$$

So a heat interaction at constant pressure will cause a change in enthalpy.

If in a constant pressure process, the heat interaction is carefully measured for a known mass of pure substance, a second specific heat term is obtained, and this is called the specific heat at constant pressure.

Thus,

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

The unit of  $c_p$  is  $\text{kJ/kg K}$  or  $\text{J/kg K}$ .

$c_p$  like  $c_v$  is also an intensive property.

$\Delta h$  depends only on  $\Delta T$  and  $c_p$ , and not on any particular heat or work interaction leading to that change.

Example Problem #1

In a process, a gas of mass 0.05 kg has heat and work interactions of -400 J and -2000 J, respectively.  $c_v$  for the gas is  $718 \text{ J/kg K}$ . calculate the temperature change of the gas during the process.

Solution:

$$\begin{aligned} \frac{Q - W}{m} &= u_2 - u_1 = c_v (T_2 - T_1) \\ Q - W &= \cancel{m} c_v \cancel{(T_2 - T_1)} = m c_v (T_2 - T_1) \\ \Rightarrow -400 - (-2000) &= 0.05 \times 718 \times (T_2 - T_1) \\ \Rightarrow +1600 &= 35.9 \times (T_2 - T_1) \\ \Rightarrow T_2 - T_1 &= 44.57 \text{ K} \end{aligned}$$

## Example Problem #2

In a constant pressure process, 0.01 kg of a gas having a  $c_v$  of 718 J/kg K increases in temperature by 300 K as its specific volume increases from 0.086 to 0.172 m<sup>3</sup>/kg at constant pressure of 1000 kPa. Calculate  $Q$  and  $W$ .

Solution: Applying the First law

for a process,

$$Q - W = U_2 - U_1$$

Now,

$$\begin{aligned} W &= P (V_2 - V_1) \\ &= 1000 \times 10^3 (0.172 - 0.086) (0.01) \\ &= 860.0 \text{ J} \end{aligned}$$

$$\begin{aligned} U_2 - U_1 &= m c_v (T_2 - T_1) \\ &= 0.01 \times 718 \times 300 \\ &= 2154.0 \text{ J} \end{aligned}$$

(21)

Hence,

$$Q - 860 = 2154$$

$$\Rightarrow Q = +3014.5$$

for the constant pressure process.

$$Q = m C_p (T_2 - T_1)$$

$$\Rightarrow C_p = \frac{Q}{m (T_2 - T_1)}$$

$$= \frac{3014}{(0.01)(300)}$$

$$= 1004.7 \text{ J/kg K}$$

$c_p$  is always greater than  $c_v$ ; why?

The specific heat at constant pressure ( $c_p$ ) is always greater than  $c_v$  because at constant pressure the system is allowed to expand and the energy for this expansion work must also be supplied to the system.

Points  
Important / to Note reg. use of  $c_p$  and  $c_v$

$c_v$  and  $c_p$  should be thought of in terms of their definitions as certain partial derivatives. Only in special processes (constant volume or constant pressure)  $c_v$  and  $c_p$  are related to energy transfer as heat.

## Internal Energy of a Real Gas

Imagine a thermally insulated vessel with rigid walls, divided into two compartments by a partition. Suppose that there is a gas in one compartment and that the other contains a vacuum. If the partition is removed, the gas will undergo what is known as an adiabatic free expansion in which no work is done and no heat is transferred. From the first law, since both  $Q$  and  $W$  are zero, it follows that the internal energy remains unchanged during a free expansion.

The question of whether or not the temperature of a gas changes during a free expansion and, if it does, of the magnitude of the temperature change has engaged the attention of scientists for about a hundred years. Starting with Joule in 1843, many attempts have been made to

(2)

measure either the quantity  $(\partial T / \partial V)_U$ , which is called the Joule coefficient, or related quantities that are all a measure, in one way or another, of the effect of an adiabatic free expansion, or as it is often called, Joule expansion.

Internal Energy of an Ideal Gas: Joule's Experiment

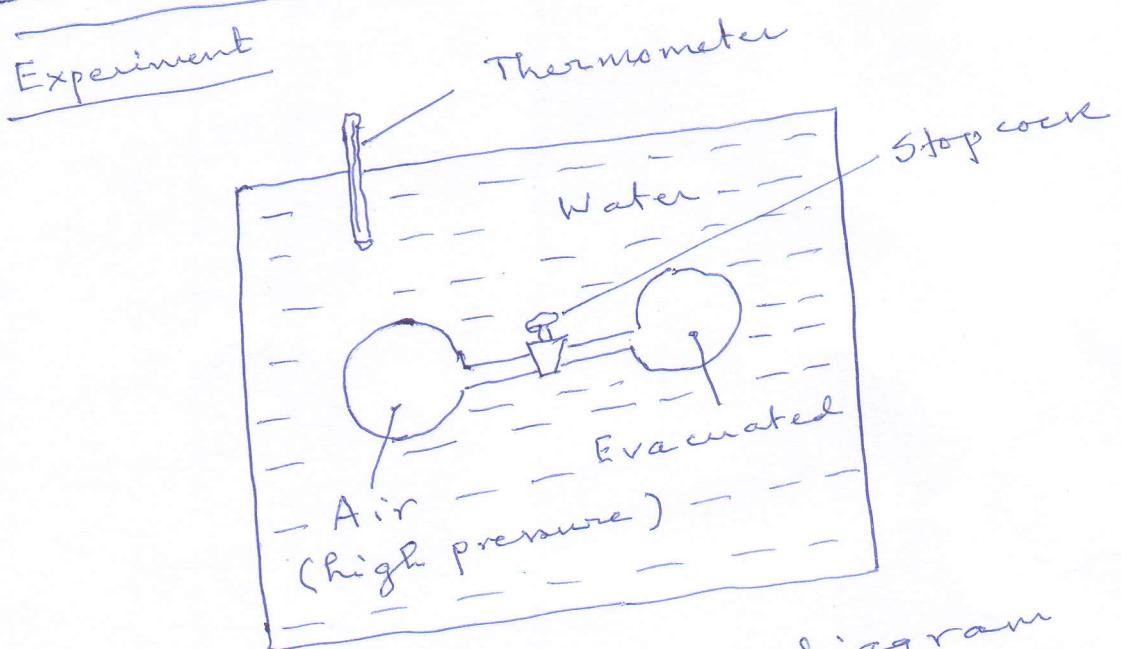


Fig. 1 Schematic diagram of the experimental apparatus used by Joule

In order to study the free expansion of a gas and to measure  $(\partial T / \partial V)_U$ , Joule connected two vessels by a

short tube and stopcock (Fig. 1), which were immersed in a water bath. One vessel contained air at high pressure, and the other was evacuated. The temperature of the water was measured before and after the expansion, the idea being to measure indirectly the drop in temperature of the gas from the decrease in temperature of the water. Since the heat capacity ( $\mathfrak{C}$ ) of the vessels and the water was approximately 1000 times as large as the heat capacity of air, Joule was unable to detect any temperature change of the water, although in the light of our present knowledge, the air must have undergone a temperature decrease of several degrees. A direct measurement of the temperature change associated with a free expansion is so difficult that it is necessary to give up directly measuring the Joule coefficient  $(\partial T / \partial V)_U$ .



(5)

If no temperature change ( $dT = 0$ ) takes place in a free expansion ( ~~$\delta Q = 0$~~   $du = 0$ ), then it follows that (A)

$$\left(\frac{\partial u}{\partial P}\right)_T = 0$$

or, in other words,  $u$  does not depend on  $P$ .

Then, it is apparent that, if no temperature change takes place in a free expansion of a gas,  $u$  is independent of  $v$  and  $P$ , and is independent of  $T$  only.

Therefore,  $u$  is a function of the internal energy only. Thus, to determine if the internal energy is a function of temperature, one must perform an experiment where the temperature is constant and measure whether  $(\partial u / \partial T)_P$  or  $(\partial u / \partial P)_T$  is zero.

(6)

We have seen that, in the case of a real gas, only in the limit as pressure approaches zero does the equation of state assume the simple form  $PV = RT$ .

Furthermore, the internal energy of a real gas is a function of pressure as well as temperature. It is convenient at this point to define the ideal gas whose properties, while not corresponding to those of any existing gas, are approximately those of a real gas at low pressures. By definition, the ideal gas satisfies the equations

$$PV = RT \quad (5)$$

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \quad (6)$$

The requirement that  $(\partial U / \partial P)_T = 0$  may be written in other ways.

$$\text{Thus, } \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

and since  $(\partial P / \partial V)_T = -RT / V$   
 $= -\frac{PV}{V^2} = -\frac{P}{V}$ , and therefore, is  
 not zero, while  $(\partial U / \partial P)_T$  is zero,

(7)

it follows that for the ideal gas

$$\left( \frac{\partial u}{\partial v} \right)_T = 0 \quad (7)$$

Finally, since both  $(\partial u / \partial p)_T$  and  $(\frac{\partial u}{\partial v})_T$  are zero,  $u = f(T)$  only. (8)

Whether a real gas may be treated as the ideal gas depends upon the error that may be tolerated in a given calculation. A real gas at pressures below about twice standard atmospheric pressure may be treated as the ideal gas without introducing an error greater than a few percent. Even in the case of a saturated vapor in equilibrium with its liquid, the ideal-gas equation of state may be used with only a small error if the vapor pressure is low.

## Enthalpy of Ideal Gases

$$\begin{aligned} h &= u + Pv \\ Pv &= RT \end{aligned} \quad \left. \begin{aligned} h &= u + RT \\ h &= h(T) \end{aligned} \right\}$$

Since  $R$  is a constant and  $u = u(T)$ , it follows that (9)

$$h = h(T) \text{ only}$$

specific Heats of Ideal Gases  
Since  $u$  and  $h$  depend on temperature for an ideal gas, the specific heats  $c_p$  and  $c_v$  also depend, at most, on temperature only. Therefore, replacing the partial derivatives in the definitions of  $c_p$  and  $c_v$ , we can write (10)

$$du = c_v(T) dT$$

$$\text{and } dh = c_p(T) dT$$

$$\text{Thus, } \Delta u = u_2 - u_1 = \int_1^2 c_v(T) dT \quad (12)$$

$$\text{and } \Delta h = h_2 - h_1 = \int_1^2 c_p(T) dT \quad (13)$$

(9)

At low pressures, all real gases approach ideal-gas behaviour, and therefore, their specific heats depend on temperature only.

$u$  and  $h$  data for a number of gases have been tabulated over small temperature intervals. These tables are obtained by choosing an arbitrary reference point and performing the integrations in eqs. (12) and (13) by treating state 1 as the reference state, and both  $u$  and  $h$  are assigned zero values at that state (Table 1). The choice of reference states have no effect on  $\Delta u$  and  $\Delta h$  calculations.

Air Table 1

$T(K)$	$u (kJ/kg)$	$h (kJ/kg)$
0	0	0
1	214.07	300.19
300	221.25	310.24
310	1	1
1	1	1

(10)

Accurate analytical expressions for ideal-gas specific heats, based on direct measurements are available and given as third degree polynomials for several gases (Table A-2c of the textbook).

$$\bar{C}_p = a + bT + cT^2 + dT^3 \quad (14)$$

$\bar{C}_p$  in  $\text{kJ}/\text{kmole K}$   
( $T$  in K, and  $\bar{C}_p$  in  $\text{kJ}/\text{kmole K}$ )

At low pressures  $\bar{C}_p$  and  $\bar{C}_v$  are often denoted by  $\bar{C}_p^0$  and  $\bar{C}_v^0$ , respectively.  $\bar{C}_p^0$  vs.  $T$  graphs have been plotted for  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , Air and  $\text{H}_2$  as well as  $\text{Ar}$ ,  $\text{He}$ ,  $\text{Ne}$ ,  $\text{Kr}$ ,  $\text{Xe}$ ,  $\text{Rn}$  <sup>(radon)</sup> in Fig. 2.

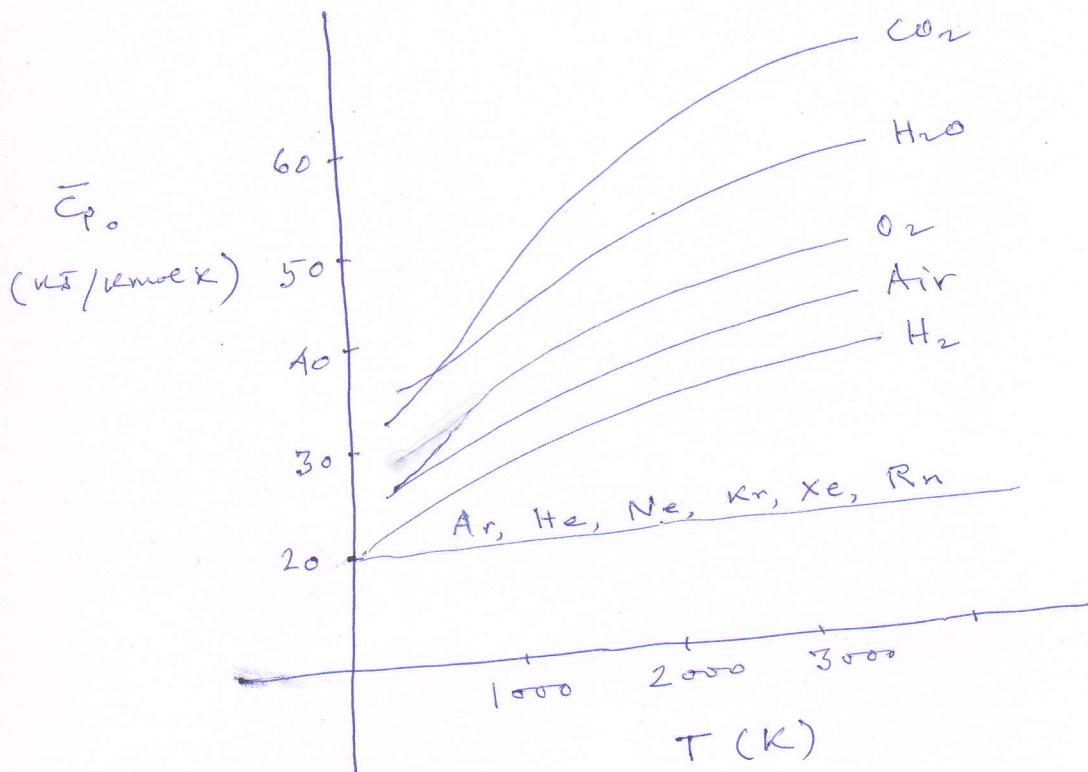


Fig. 2 Ideal-gas constant pressure specific heats for some gases  
 $(\bar{C}_p = a + bT + cT^2 + dT^3)$

Fig. 2 reveals that the specific heats of gases with complex molecules (molecules with two or more atoms) are higher and increase with temperature. Also, the variation of specific heats with temperature is smooth and may be approximated as linear over small temperature intervals (a few hundred degrees or less). Therefore, the specific

(12)

heat functions in eqs.(12) and (13) can be replaced by the constant average specific heat values. Then, the integrations in these equations can be performed,

yielding

$$u_2 - u_1 = c_v, \text{avg} (T_2 - T_1) \quad (15)$$

$$h_2 - h_1 = c_p, \text{avg} (T_2 - T_1) \quad (16)$$

and