School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020

Lecture TOPIC 3 (Finn: 3.1, 3.2, 3.3, 3.4, 3.6)
Synopsis: Heat, work, Internal energy, heat capacities and the First Law: $\Delta U = \Delta Q + \Delta W$.

FIRST LAW OF THERMODYNAMICS: Conservation of Energy

> Clausius: *In all cases in which work is produced by the agency of heat, a quantity of heat is consumed which is proportional to the work done; and conversely, by the expenditure of an equal quantity of work an equal quantity of heat is produced.*

INTERNAL ENERGY

Joule's experiments (1840-1849) confirmed the measurements of Benjamin Thompson (Count Rumford) that heat could be produced by mechanical work alone. Joule produced work from falling weights suspended over pulleys attached to paddles in a thermally insulated tub of water. For a given mass of water, the same amount of work was always needed to produce a one degree rise in temperature. This was the mechanical equivalent of heat: 4.2×10^3 J kg^{-1} K^{-1} in SI units. The same value was found from dissipation of energy in a current-carrying resistor ('immersion heater') for which the source of energy could also be traced back to mechanical generation with a 'dynamo'. These experiments illustrate a general principle:

> *If a thermally ISOLATED system is brought from one equilibrium state to another, the work necessary to achieve this change is independent of the process used.*

The above observation suggests that there is a state function U, the internal energy, for which $U_2 - U_1 = W_{adiabatic}$ = work done adiabatically to make the change between initial (1) and final (2) equilibrium states. This is a restricted form of the First Law of Thermodynamics.

EQUIVALENT PROCESSES

We can apply the main postulate and the zeroeth law to calculate the final temperature when cold ice is dropped into hot water. The equilibrium state has equal temperature throughout, and because temperature is a state variable, we can use *any* process to calculate it. We do *not* need to worry about how it happens.

- The water cools to $0°$.

- The ice warms to $0°$.

- The ice melts.

- Everything warms up again.

We implicitly assume that the energy of these heat flows go into some unspecified storage reservoir. Then, the sum of them is put back into the system to warm the water back up from $0°$ to its final temperature, or refreeze some ice. In reality, there is no storage reservoir: this is an example of using an *equivalent* process to make a thermodynamic problem mathematically tractible. It is legitimate because temperature and internal energy are state variables.
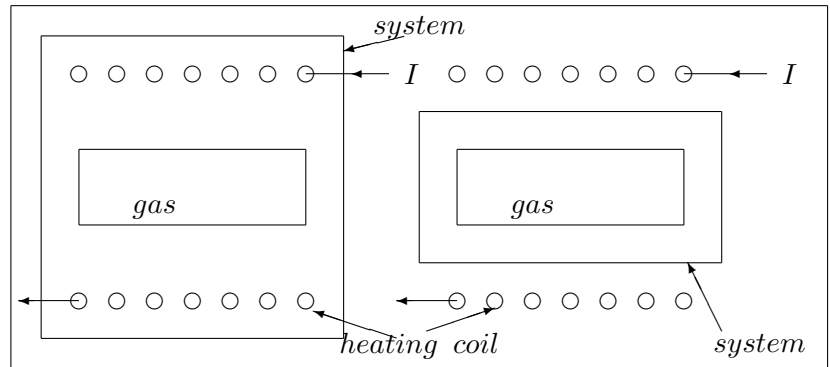
HEAT

More generally, if system is not thermally isolated, $W \neq U_2 - U_1$ (topic 03). This can be taken into account by writing $U_2 - U_1 = W + Q$, where Q is the energy transfer which cannot be accounted for in terms of work, defined so that Q is positive for heat going **INTO** the system:

> *Heat is the exchange of energy between the system and the surroundings that cannot be identified as work (eg mechanical work).*

Illustration of the difference between WORK and HEAT

In the left image below the electrical heating element is included in the system and energy is supplied as work $(I.V)$ whereas in the right image the heating element is outside the system and energy is supplied as heat.

This leads to the general statement of the First Law of Thermodynamics, for infinitesimal changes: $dU = \dbar W + \dbar Q$, where both $\dbar W$ and $\dbar Q$ are path-dependent. For a compressible fluid, the statement of the First Law for infinitesimal reversible processes is:

$$dU = -PdV + \dbar Q$$

THE HEAT CAPACITY (C) OF A SYSTEM

Definition

$$C = \frac{\text{Heat in}}{\text{Temperature rise}} = \lim_{\Delta T \to 0} \left(\frac{Q}{\Delta T} \right) = \frac{dQ}{dT}$$

Specific heat capacity is $c = \frac{1}{m}C$, where m is the mass of the system. Molar heat capacity often also called the "molar specific heat capacity" is often denoted by the same symbol: $c = \frac{1}{n}C$, where n is the number of moles of molecules in the system.)

Heat capacity at constant volume, C_V

For $V = $ constant, $dV = 0$ and First Law gives $dU_V = 0 + dQ_V$, from which

$$C_V = \frac{dQ_V}{dT} = \frac{dU_V}{dT} = \left(\frac{\partial U}{\partial T} \right)_V$$

partial derivative since U might depend on more than just temperature T.

Heat capacity at constant pressure, C_P

The First Law now gives $dQ_P \neq dU_P$, because V will change ($dV \neq 0$) and work is done. However, for $P = $ constant, it is convenient to define *Enthalpy*: $H = U + PV$

$dH_P = d(U+PV) = dU + PdV + \cancel{VdP} = -PdV + dQ_P + PdV = dQ_P$

So

$$C_P = \frac{dQ_P}{dT} = \frac{dH_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

$H = U + PV$ (with the units of energy) is a useful function for treatment of constant pressure processes and more generally to describe changes where the pressures of the initial and final states are known.

Notice that Heat Capacity is a State Variable (unlike Heat).

Relation between C_p and C_V

$C_p - C_V$ for an ideal gas

The energy of n moles of an ideal gas is $n\frac{3}{2}N_A k_B T$, where N_A is Avogadro's number and k_B is Boltzmann's constant. So for an ideal gas U is a function of T only: $U = U(T)$. Then writing $U = U(T, V)$,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT \qquad \text{Ideal gas only}$$

$$dU = C_V dT \qquad \text{Ideal gas only}$$

That means that dU may be replaced by $C_V dT$ in subsequent analysis for an ideal gas. Thus, using the First Law ($dQ = dU + pdV$),

$$C_p = \frac{dQ_P}{dT} = C_V + P\left(\frac{\partial V}{\partial T}\right)_P = C_V + nR \qquad \text{Ideal gas only}$$

$C_p - C_V$ for any fluid

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{1}$$

We want to express $(\partial U/\partial T)_P$ in terms of $C_v = (\partial U/\partial T)_V$. Therefore use U(T,V):

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = C_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Substituting this in EQN 1 gives,

$$C_p - C_V = \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)\left(\frac{\partial V}{\partial T}\right)_P,$$

which is our final general result. The relation for an Ideal gas can be recovered noting $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and calculating $\left(\frac{\partial V}{\partial T}\right)_P$ from the ideal gas equation of state $PV = nRT$.

WORK

Reversible Isothermal Expansion of an Ideal gas (No temperature change)

The equation of state $PV = nRT$ gives $P = nRT/V = \text{constant}/V$ with different values of the constant for different temperatures (ie a family of hyperbolae). The work done on the surroundings by a system comprising n moles of ideal gas expanding reversibly and isothermally is equal to $nRT\ln(V_2/V_1)$.

Reversible Adiabatic Expansion of an Ideal gas (No heat transfer)

For a reversible process, P is well defined and so we can write dW as an integral $-\int P dV$. The First Law gives $dQ = dU + P dV = C_V dT + P dV$.

 Adiabatic means $dQ = 0$. So $-P dV = C_V dT$.

 Then substitute for P from the ideal gas equation, giving $(nR/V)dV = (C_v/T)dT$. Finally integrate both sides and use $C_P - C_v = nR$ to obtain

$$TV^{\gamma-1} = \text{a constant}, \qquad \text{where } \gamma = C_P/C_V$$

The equation describes the variation of T with V in a reversible adiabatic process. Alternative equations (use the ideal gas equation to derive them) are:

 $PV^{\gamma} = $ a different constant
 $TP^{1-\frac{1}{\gamma}} = $ yet another constant

 For a reversible adiabatic expansion, from (P_i, V_i) to (P_f, V_f), the work done on an ideal gas, by its surroundings is $dW = -\int P dV = \int C_V dT = C_V(T_f - T_i)$.

 For an irreversible process, this expression for work is *not* true because pressure of the gas is not well defined, so nor is the integral for work $\int P dV$. BUT the change in internal energy $\Delta U = C_V(T_f - T_i)$ *is* correct because U, C_V and T are all state variables.
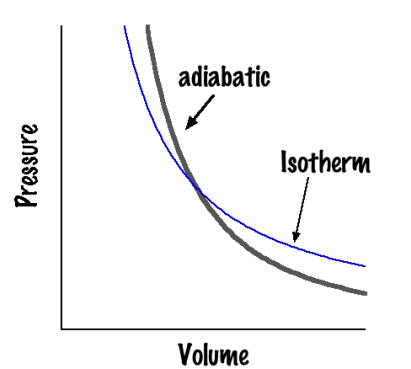
Irreversible Adiabatic Expansion and Free Expansion (Joule) Coefficient

Consider a container with rigid adiabatic outside walls. An inner rigid partition divides the container into two equal volumes V with gas initially occupying only one of the volumes and a vacuum in the other. The system is the combination of gas plus vacuum inside the outer wall. The partition is then broken and the gas moves **irreversibly**, into the vacuum, until the two halves each contain the same amount of gas. The system does no work on its surroundings, and no heat enters the system from its surroundings. Therefore the final internal energy of the gas, has to be equal to the initial value. To find the change in temperature, write $T = T(U, V)$. Then

$$dT = \left(\frac{\partial T}{\partial V}\right)_U dV + \left(\frac{\partial T}{\partial U}\right)_V dU = \left(\frac{\partial T}{\partial V}\right)_U dV = \mu_J dV$$

 μ_J is the Joule coefficient, whose value depends on the gas being used, and can be predicted from the gas's equation of state. For a free expansion of a gas from V_i to V_f, the temperature change can be calculated from $\Delta T = \int_{V_i}^{V_f} \mu_J dV$.

 For an ideal gas, internal energy depends only on temperature (U=U(T)) and vice versa (T=T(U)), $\mu_J = 0$, so the final temperature will be the same as the initial temperature.

 For a real gas, intermolecular forces depend on how far apart the molecules are, so U is a function of both T and V.