The first law of thermodynamics

THE FIRST LAW OF THERMODYNAMICS, THE CONCEPTThe First Law: the conceptsThe basic conceptsA system is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, and so on. Around the system is its surroundings, where we make our observations. The two parts may be in contact and are separated by a boundary, and specifying the system and its surroundings amounts to careful specification of the boundary between them.

When matter can transfer through the boundary between system and its surroundings the system is open; otherwise it is closed. An isolated system is closed system that has neither mechanical nor thermal contact with its surroundings. Work, heat, and energyWork, heat, and energy are the basic concepts of thermodynamics, and of these the most fundamental is work. As we shall see, all measurements of heat and changes in energy amount to measurements of work. Work is done during a process if that process could be used to move an object certain distance or to change its height. W = F x d = m g h (J). We shall say that work is done by the system if a weight has been raised up in the surroundings and it is given a negative sign (-ve) and this work = – mgh (you may imagine your hand is the system which will raise certain weight). The work has been done on the system when a weight has been lowered down and it is given a positive sign (+ve) and this work = mgh.

When we need to measure the amount of work we use its definition as force ? distance. Energy is the capacity of a system to do work. When the energy of a system changes as result of a temperature difference between it and its surroundings we say that energy has been transferred as heat. When

a beaker of water (the system) stands on hot plate, the capacity of the system to do work increases, so its energy has increased; since the increase has occurred as result of a temperature difference, that energy has been transferred to the system as heat. Not all substances permit the transfer of energy even though there is a temperature difference between the system and its surroundings.

Walls that do permit energy transfer as heat (such as steel and glass) are called diathermic (dia is the Greek word for " through). Walls that do not permit energy transfer as heat are called adiabatic. A Dewar flask is a good approximation to an adiabatic container. A process that releases energy as heat is called exothermic. All combustion reactions are exothermic.

Processes that absorb energy as heat are called endothermic. An example is the vaporization of water. The First LawFrom now on, we shall call the total energy of a system its internal energy U. It is impossible to know the absolute value of the internal energy of any system, but in thermodynamics we deal only with changes in the internal energy. We shall denote by ? U the change in internal energy when a system changes from an initial state (i) with internal energy Ui to a final state (f)with internal energy Uf is ? U = Uf – UiThe internal energy is a state property in the sense that its value depends only on the current state of the system, and is independent of how that state has been prepared. Other examples of state properties are temperature, pressure, and density. Path property which depends on the path as work w and heat q never written as ? w or ? q but dw and dq. The internal energy is also an extensive property, a property that depends on the size (extent) of the system.

Thus, the internal energy of 2 kg of water is twice that of 1kg of water at the same temperature and pressure. Other examples of extensive properties include mass and volume. In contrast, the temperature of a system is an intensive property, for it is independent of the size of the system, and 2kg of water has the same temperature as 1kg of water taken from the same source.

Other examples of intensive properties are the density, the pressure, and all molar quantities, such as the molar volume and the molar internal energy, the internal energy per mole. Internal energy, heat, and work are all measured in the same unit, the joule (J), We shall normally express changes in internal energy in kilojoules, where 1kJ = 103 J and changes in molar internal energy in kJ mol-1. The conservation of energyExperiments have established two further characteristics of the internal energy. The first is that the internal energy of an isolated system is constant (no heat or work in or out). This observation is often summarized by the remark that ? energy conserved ?.

The second characteristic of internal energy is that whereas we may know how energy has been transferred the system is blind to the mode employed (only need initial and final states). Heat and work are equivalent ways of changing a systems energy: energy is energy; however it is gained or lost. A thermodynamic system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy. These two characteristics of the internal energy are summarized in a statement called First Law of thermodynamics: ??? The internal energy of a system is constant unless it is changed by doing work or by heating???. If we write w for the work done on

a system, q for the energy transferred as heat to it, and ? U for the resulting change in internal energy, the mathematical form of the First Law is For infinitesimal changes in q and w, dU = dq + dwThis equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat and work. If none passes through (when the system is isolated), then ? U = 0Note: q as mentioned here represents only the transferred heat from system to surrounding or from surrounding to system and it does not represent the thermal energy content of the system. For example in compression adiabatic process the heat transferred q = 0, but there is an increase in temperature which will increase the thermal energy and the internal energy of that system.

Example: Calculating a change in internal energyA certain electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each secondAnswer: Since energy is lost from the system as work, w is negative, and w = -15 kJ. Energy is also lost as heat, so q = -2 kJ. The total change in internal energy is therefore? U = -2 kJ ??" 15 kJ = -17 kJComment: If we had decided to call the motor alone the system, then its internal energy would not have changed: the motor lost 17 kJ to the surroundings but the power supply did 17 kJ of work on the motor.

The net loser is the power supply; the motor is a device that converts one form of energy into another. NotesWhen the work done on the system w is Positive, and if energy given to system & q is also positive. If the system does the work or heat loss, to surrounding w & q are both negative. The work in expansion process is negative and T decreases (if the process is not

isothermal), and work in compression process is positive and T increases(if the process is not isothermal),. Infinitesimal changesWe can open the way to powerful methods of calculation by switching attention to infinitesimal changes of state (such as infinitesimal changes in temperature) and infinitesimal changes in the internal energy dU. Then, if the work done on a system is the infinitesimal amount dw and the energy supplied to it as heat is dq, in place of ? U= q + w we have: dzArea ApexpWhen a piston of area A moves out through a distance dz , it sweeps out a volume dV = Adz. The external pressure pex is equivalent to a weight pressing on the piston, and the force opposing expansion is F = pexA.

Work of compression and expansionIn thermodynamics we are often concerned with the work done on or by a system. This can be calculated by considering the arrangement shown in figure, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A. If the external pressure is pex, the force on the outer face of the piston is: (pex A) pressing down on the system . We shall suppose that the motion of the piston is quasistatic, or slow.

Quasistatic motion ensures that the surroundings are in internal equilibrium. When the system expands quasistatically through a distance dz, it raises the weight pex A through a distance dz, so the work done is dw = – pex A ? dz. The work done by a gas when it expands against a constant external pressure is equal to the shaded area in this indicator diagram.

But A dz is the volume swept out in the course of the expansion, which we write dV (dV in case of expansion is positive). Therefore, the work done when

the system expands through dV against a constant pressure pex is: . If instead the system is compressed, the work done on the system is given by the same equation but in compression dV is negative (a reduction of volume) and so dw is positive.

Work is done on the system by compression and so long as no other energy changes take place, its internal energy rises. Here we can come to important conclusion that the general form of work for either compression or expansion is: Free expansionVfFree expansion occurs when pex = 0, hence work = 0. Which means that no work is done, and dw = 0 for each stage of the expansion. Expansion against constant pressureSince the external pressure pex is constant through the expansion (e. g., the piston is pressed on by the atmosphere of the outside world), the work done as the system passes quasistatically through each successive infinitesimal displacement dV is dw = – pex dV .

The total work done in the expansion from Vi to Vf is the sum of all these equal contributions: Therefore, writing the change in volume as ? V = Vf – Viw = -pex ? VThis result is illustrated graphically in the figure above: the magnitude of w is equal to the area beneath the horizontal line at p = pex (which means p is constant) lying between the initial and final volumes. Reversible expansionA reversible change in thermodynamics is a change that can be reversed by an infinitesmal modification of a variable as for example if we have a cylinder contains gas and it is fitted with a piston and a pile of sand was put on the top of this piston to prevent the gas from expansion then the sand was removed particle by particle to allow the gas to

expand reversibly. We say that for a reversible change a system is always in equilibrium with its surroundings.

Suppose the gas which is confined by the piston has an external pressure pex is set equal to the pressure of the confined gas p. Such as a system is in mechanical equilibrium with its surroundings, since an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions. If the external pressure is made infinitesimally less than the internal pressure (by removing some sand particles), the gas expands slightly and the gas pressure decreases to be equal to the external pressure.

If the external pressure is increased infinitesimally (by adding some sand particles), gas is compressed slightly and hence its pressure increases. In either case the internal pressure changes to be equal to the external pressure at each step and this change is reversible in the thermodynamic sense. To achieve reversible expansion (mechanical equilibrium) we must match pex to p at each stage: d w = -pex dV = -p dVAlthough the pressure inside the system appears in this expression for the work, it does so only because pex has been set equal to p to ensure reversibility. The total work of reversible expansion is therefore . P here is for the gas inside the cylinder and we can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Reversible expansion may be summarized as follows: 1) It occurs by an infinitesimal changes.

2) Equilibrium between system & surrounding is established at each step. 3) Pex = Pinternal at each step and hence d w = -pex dV = -p dV. 4) Max work is obtained and equal = the area under the P versus V curve which is a

smooth one in case of reversible process only. Isothermal reversible expansionWe shall illustrate the use of an equation of state to evaluate the work by considering the isothermal reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with the surroundings (such as a constant temperature bath). Since the equation of state is $pV = nRT$, we know that at each stage $p = nRT/V$, with V the current volume. The temperature T is constant in an isothermal expansion, and so may be taken outside the integral.

It follows that: $dw = -p_{ex}dV = -p \, dV$ (for reversible process $P_{ex} = P$), $p = nRT/V$ and hence $w = -nRT \ln (V_f/V_i)$, for Isothermal Reversible Expansion or Compression When the final volume is greater than the initial volume, as in an expansion, the logarithm in the last equation is positive and hence $w < 0$. In this case, the system has done work on the outside world. We obtain more work when the expansion is reversible because matching the external pressure to the internal pressure at each stage ensures that none of the systems pushing power is wasted. We cannot obtain more work than the reversible amount because increasing the external pressure even infinitesimal results in contraction.

Example: Calculating the work of gas productionCalculate the work done when 50g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25?°C. Answer. In (a) the volume cannot change, so no work is done ($dV = 0$) and $w = 0$.

In (b) the gas drives back the atmosphere (constant pressure) and therefore $P_{ex} = P = $ constant and and hence $w = -p_{ex} \, ? \, V$. We can neglect the initial

volume because the final volume (after the production of gas) is so much larger and ? V = Vf – Vi ? Vf = nRT/pex where n is the amount of H2 produced. Therefore, w= – n R TThis equation is applied to calculate the work when solid or liquid produces gas at constant pressure as in this example and as in the case of vaporization process. Since the reaction is $Fe(s) + 2HCl(aq) > FeCl_2(aq) + H_2(g)$, i. e. 1 mol $H_2(g)$ is generated when 1 mol Fe(s) is consumed, and n can therefore be taken as amount of Fe atoms that react.

Since the molar mass of Fe is 55. 85g mol-1, The system,(the reaction mixture), does 2. 2 kJ of work driving back the atmosphere. Heat and enthalpyIn general, the change in internal energy of a system is $dU = dq + dw$, and if we put $dw = dw_{exp} + dw_e$, which means that the work consists of expansion work dw_{exp} plus any other additional type of work except expansion dw_e, hence: $dU = dq + dw_{exp} + dw_e$. For instance, dw_e might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, and so $dw_{exp}= 0$. If the system is also incapable of doing any other kind of work, $dw_e= 0$ too.

Under these circumstances: $dU = dq$ at constant volume, no additional work. We express this by writing $dU = dq_V$. Hence, in measuring the energy supplied to a constant-volume system as heat (q> 0) or obtained from it (q