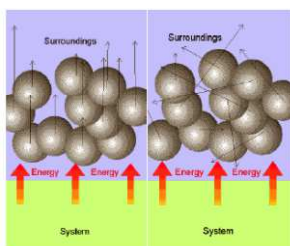


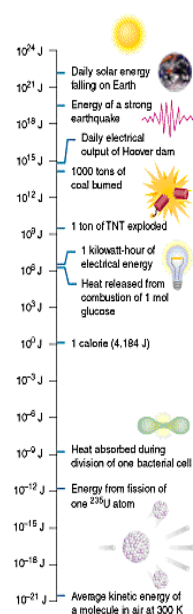
Lecture 5

Basic Thermodynamics. The First Law



References.

- Chemistry³, Chapter 14, Energy and Thermochemistry, pp.658-700.
- Elements of Physical Chemistry, 5th edition, Atkins & de Paula, Chapter 2, Thermodynamics: the first law, pp. 41-62.
- Physical Chemistry, 8th Edition, Atkins & de Paula, The First Law, Chapter 2, pp.28-75.
- Chemistry and Chemical Reactivity, Kotz, Treichel, Townsend, 7th edition, Chapter 5, pp.208-253.



Typical energy estimates

Thermodynamics : some general comments

<http://en.wikipedia.org/wiki/Thermodynamics>

Thermodynamics is concerned with energy transformations in chemical and physical systems.

Thermodynamics is an experimental science based on a small number of principles that are generalizations made from experience.

Thermodynamics is concerned with the macroscopic or large scale properties of matter and makes no hypothesis about the small scale or microscopic structure of matter. The latter is the domain of Statistical Thermodynamics.

Chemical Thermodynamics deals specifically with chemical systems and provides criteria for determining whether or not a particular chemical reaction will proceed, and if it does, to what extent.

Basic Definitions

Energetic transformations take place within regions of space. A specified collection of material particles enclosed in a specified real or hypothetical boundary is said to constitute a thermodynamic system.

The surroundings or environment is labelled as any region outside the system.

We do our measuring in the surroundings.

The system and surroundings are separated by a boundary.

In an isolated system there is no transfer of either energy or matter between the system and the surroundings.

In a closed system there is transfer of energy but not of matter across the system/environment boundary.

In an open system both energy and matter can be transferred between the system and the surroundings.

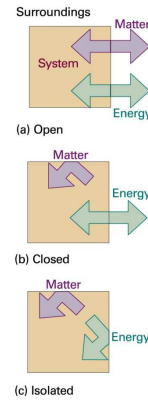
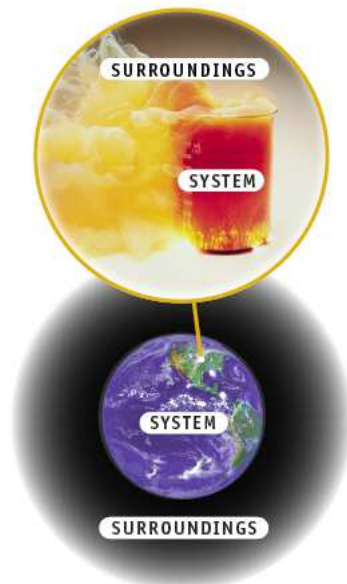


Fig. 2.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.



- **SYSTEM**
 - The object under study
- **SURROUNDINGS**
 - Everything outside the system

Work, Heat and energy

Kotz, section 5.1, pp.209-214.
Chemistry³, section 14.1, pp.660-666.

Energy: Energy is defined as the capacity to do work. Work and heat are two fundamental ways by which energy may be transferred to or from a system, and so the energy of a system can be changed by work and heat. Units: joules (J) or kJ mol^{-1} .

Work: Work is a form of energy which can transfer in and out of a system, that is stored in the organized motion of molecules. Work is done when an object is moved against some opposing force.

Heat: Heat is a form of energy which can transfer in and out of a system that is stored in the random motion (thermal motion) of molecules. If an energy difference of a system results from a temperature difference between it and the surroundings, energy has been transferred as heat.

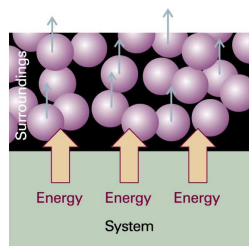


Fig. 2.4 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

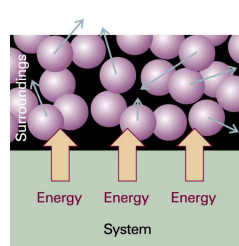


Fig. 2.3 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

Thermodynamic definitions of work and heat.

The system may be thought of as an energy bank. Transactions with the bank can be made in two kinds of currency – work and heat. Once the currencies are inside the bank they are stored simply as energy reserves and may be withdrawn in any currency.

Thermodynamically speaking heat and work are not forms of energy but are processes by which the total energy (the internal energy) of a system is changed.

The quantity of energy transferred as work during a transaction with the system is denoted as W (units: J or kJ). Work done on the system is regarded as positive since the latter work results in an increase in the energy of the system. In contrast the work done by the system is negative due to the fact that the system loses energy by doing work on the surroundings.

The total energy of a system at any given time is termed the internal energy U (or E).

It comes from the total kinetic and potential energy of the molecules which compose the system.

Heat q (units: J or kJ) is energy which is transferred across the boundary of a thermodynamic system during a change in its state by virtue of a difference in temperature between the system and its surroundings. When heat is transferred to the system, q is positive, since the heat transfer process results in an increase in the internal energy of the system. If heat energy is transferred from the system, q is negative, because the internal energy decreases.

Directionality and extent of heat transfer.

Energy transfer as heat occurs spontaneously from an object at a higher temperature to an object at a lower temperature.

Transfer of energy as heat continues until both objects are at the same temperature, and thermal equilibrium is achieved.

After thermal equilibrium is attained the object whose temperature has increased has gained thermal energy and the object whose temperature has decreased has lost thermal energy.

Directionality of heat transfer is described as exothermic or endothermic.

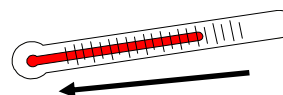
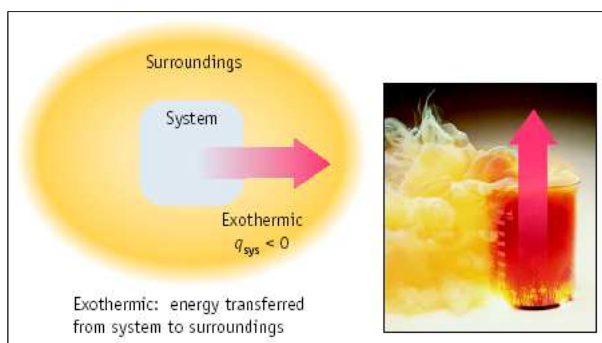
In an exothermic process thermal energy is transferred from a system to its surroundings.

The energy of the system decreases and the energy of the surroundings increases.

In an endothermic process thermal energy is transferred from the surroundings to the system, increasing the energy of the system and decreasing the energy of the surroundings.

Directionality of Energy Transfer

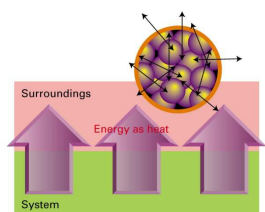
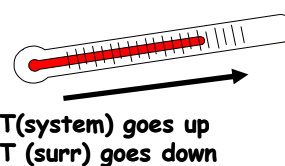
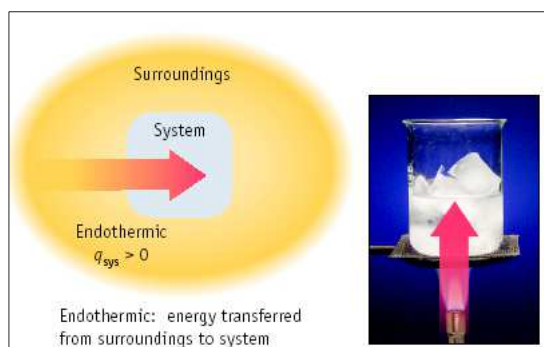
- Energy transfer as heat is always from a hotter object to a cooler one.
- **EXO**thermic: energy transfers from **SYSTEM** to **SURROUNDINGS**.



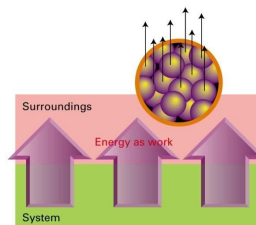
T(system) goes down
T(surr) goes up

Directionality of Energy Transfer

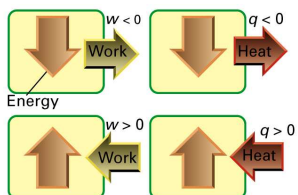
- Energy transfer at heat is always from a hotter object to a cooler one.
- **ENDO**thermic: heat transfers from **SURROUNDINGS** to the **SYSTEM**.



Heat is the transfer of energy that causes or utilizes random or chaotic motion in the surroundings.
Heat is energy which is transferred across the boundary of a thermodynamic system during a change in its state by virtue of a difference in temperature between the system and its surroundings.

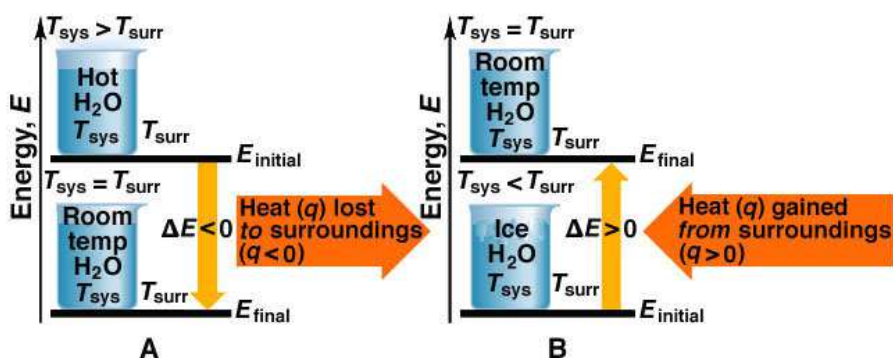


Work is the transfer of energy that causes or utilizes uniform motion of atoms in the surroundings.
Work is energy which is transferred across the boundary of a thermodynamic system during a change in its state and which can be converted completely into the 'lifting of a weight' in the surroundings (i.e., motion of a mass against opposing force).

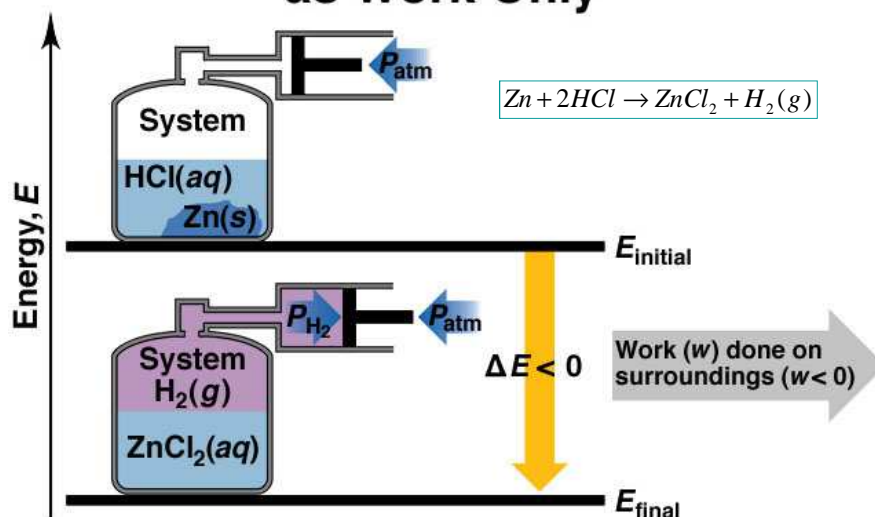


Thermodynamic sign convention:
 q and w are positive if energy enters the system (as work and heat respectively), but negative if energy leaves the system.

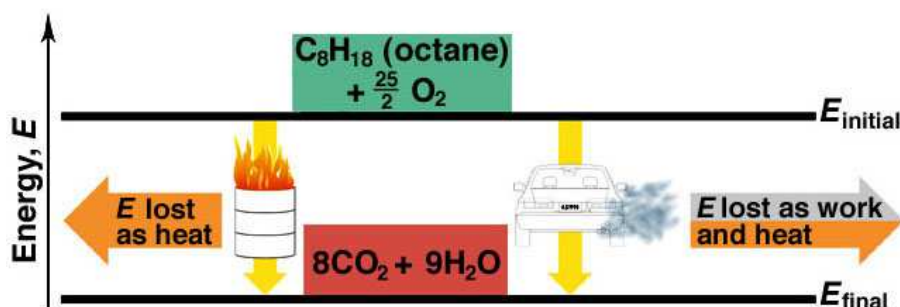
A System Transferring Energy as Heat Only



A System Losing Energy as Work Only



Two Different Paths for the Energy Change of a System



First Law of Thermodynamics: Internal energy U or E .

Internal energy (U or E): is the total energy of the system at any given time.

Comes from the total kinetic and potential energy of molecules which compose the system.

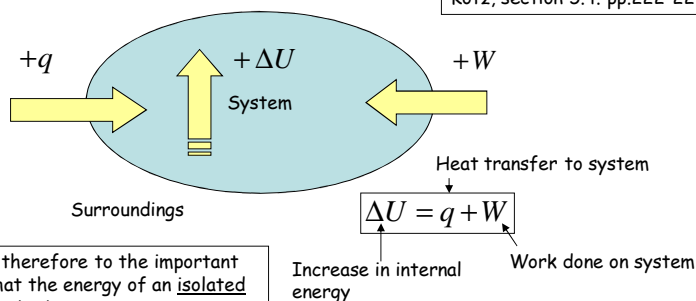
Change in internal energy (ΔU or ΔE): energy change as system goes from an initial state with energy U_i to a final state with energy U_f . Hence $\Delta U = U_f - U_i$.

We suppose that a closed system undergoes a process by which it passes from a state A to a state B . Then the change in internal energy $\Delta U = U_B - U_A$ is given by $\Delta U = q + W$.

The first law may be cast in differential form corresponding to the situation here there is an infinitesimal change in internal energy dU caused by the addition of an infinitesimal quantity of heat $d'q$ and the performance of an infinitesimal amount of work $d'w$ on the system. Hence

We can write: $dU = d'q + d'w$. We note that $d'q$ and $d'w$ are inexact differentials - they cannot be evaluated from a knowledge of the initial and final states alone.

Kotz, section 5.4. pp.222-224



We are led therefore to the important conclusion that the energy of an isolated system is constant.

In an isolated system there is no transfer of heat or work and so $q = 0$ and $W = 0$. Hence $\Delta U = 0$ hence $U = \text{constant}$.

This is a mathematical statement of the First Law of Thermodynamics.

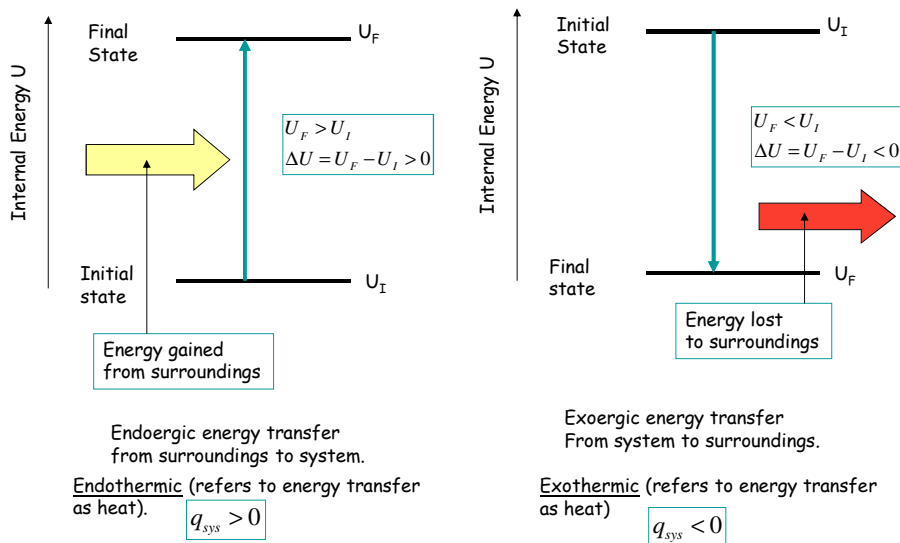
The equation $\Delta U = q + w$ is a statement of the First Law of Thermodynamics. Heat and work are equivalent forms of energy transfer and are the only ways to change the internal energy of a system. The internal energy is conserved in any thermodynamic Process in an isolated system, since for the latter both q and w are zero and so $\Delta U = 0$ or $U = \text{constant}$. Alternatively we state that in any thermodynamic process, the internal energy of the Universe is conserved, as energy is neither created nor destroyed.

$$\Delta U_{\text{universe}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0$$

| Change | Sign convention | Effect on U_{system} |
|--|-----------------|-------------------------------|
| Thermal energy transfer to system (Endothermic) | $q > 0$ (+ve) | U increases |
| Thermal energy transfer from system (Exothermic) | $q < 0$ (-ve) | U decreases |
| Energy transfer as work done on system | $W > 0$ (+ve) | U increases |
| Energy transfer as work done by system | $W < 0$ (-ve) | U decreases |

Law of conservation of energy : Total energy of the Universe is constant,

$$\Delta U_{\text{universe}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0$$



Work done in isothermal (constant temperature) expansion of a gas.

We calculate the work done when a system expands from an initial volume V_i to a final volume V_f , a change given by $\Delta V = V_f - V_i$.

Consider a piston of area A moving out through a distance h . The piston represents the moving boundary between the expanding gas and the surrounding atmosphere.

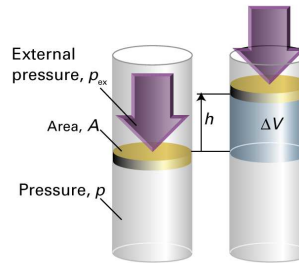
The force opposing the expansion is the constant external pressure P_{ext} multiplied by the piston area A . Hence $F = P_{\text{ext}}A$.

The work done is $w = Fh = P_{\text{ext}}Ah = P_{\text{ext}}\Delta V$.

Note that hA is the volume of the cylinder swept out by the piston as the gas expands.

We must also consider the sign of the work.

Since the system does work on the surroundings it loses energy and the work done is negative. Since ΔV is positive we need to introduce a negative sign into the work expression to ensure that w is negative when ΔV is positive. If the system is in mechanical Equilibrium with the surroundings at every stage of the expansion, Then we have a reversible expansion, the maximum Expansion work is done and $P_{\text{ext}} = P$, the gas pressure.



See AdP, Elements PChem 5, p.46 for a full discussion of Reversible expansion.

$$w = -P\Delta V$$

Reversible isothermal expansion of ideal gas.

Total work done w is given by

$$w = \int d'w = -\int_{V_i}^{V_f} P dV$$

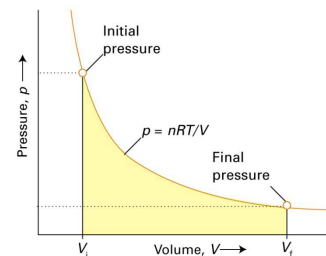
Fluid is ideal gas hence

$$P = \frac{nRT}{V}$$

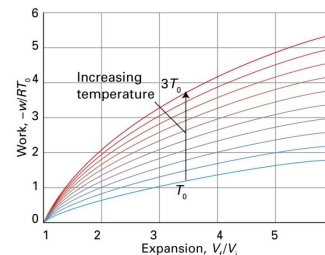
Work done:

$$w = -\int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT [\ln V]_{V_i}^{V_f} = -nRT \ln \left\{ \frac{V_f}{V_i} \right\}$$

In an expansion $V_f > V_i$ so $V_f/V_i > 1$, and $\ln(V_f/V_i)$ is positive, and w is negative since energy leaves the system as the system does expansion work.



Indicator diagram : reversible isothermal expansion of ideal gas from initial state defined by (P_i, V_i) to final state defined by (P_f, V_f) . Work done given by shaded area under curve.



For a given change of volume and fixed amount of gas, the work done is greater the higher the temperature.

In general the work done on a system is expressed as the product of a generalised Force X and a generalised displacement $d\xi$, hence $w = X.d\xi$.

| Work type | $d'w$ | comment | units |
|---------------------|-------------|---|---|
| 'PV' work | $- P dV$ | P = pressure dV = volume change | P, Nm^{-2} V, m^3 |
| Surface area change | γdA | γ = surface tension dA = area change | γ, Nm^{-1} A, m^2 |
| Length change | $f dL$ | f = tension dL = length change | f, N L, m |
| Electrical work | $E dQ$ | E = electric potential Q = electric charge | E, V Q, C |