

Thermodynamics, the First Law: the concepts

Thermodynamics – concerned with the studies of transformation of energy from heat to work and vice versa.

Originally formulated by physicists (the efficiency of steam engines).

Thermodynamics – immense importance in chemistry – energy output of chemical reactions, why reactions reach equilibrium, what their composition is at equilibrium, how reactions in electrochemical (and biological) cells can generate electricity.

Classical thermodynamics – does not depend on any models of the internal constitution of matter, can be developed and used without ever mentioning atoms and molecules.

Properties of atoms and molecules – ultimately responsible for observable properties of bulk matter.

Connection between atomic and bulk thermodynamic properties – **statistical thermodynamics**.

Branches of thermodynamics

Thermochemistry – deals with the heat output of chemical reactions.

Electrochemistry – the interaction between electricity and chemistry.

Bioenergetics – the deployment of energy in living organisms.

Equilibrium chemistry – the formulation of equilibrium constants, the equilibrium composition of solutions of acids and bases.

Conservation of energy

Almost every argument and explanation in chemistry boils down to a consideration of some aspect of a single property: the *energy*. The energy determines what molecules may form what reaction may occur, how fast they may occur, in which direction a reaction has a tendency to occur.

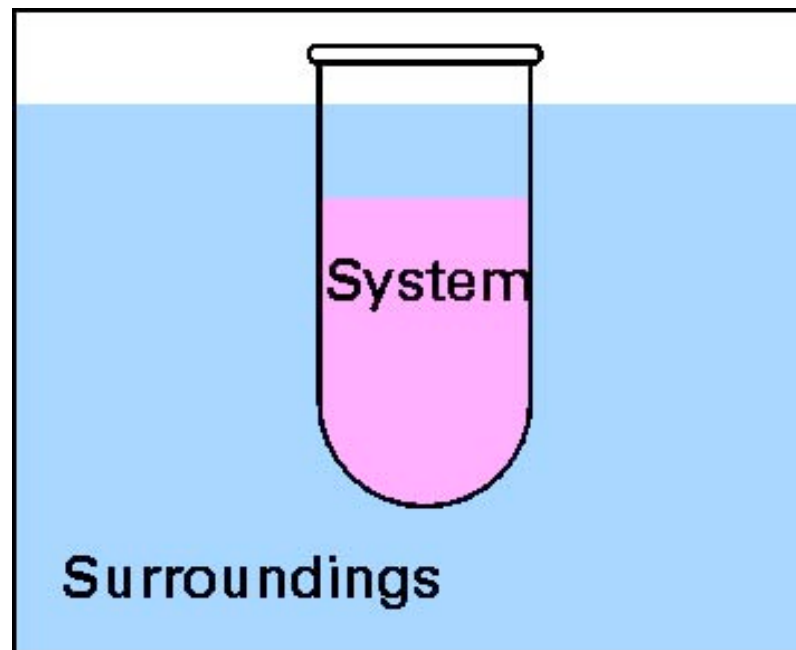
Energy – *the capacity to do work*.

Work – motion against opposing force.

A gas at high temperature has more energy than at low temperature – it has a higher pressure and can do more work in driving out a piston.

Conservation of energy – the energy can be neither created nor destroyed but merely converted from one form to another or moved from place to place.

Chemical reactions release or absorb energy – the *conversion* of energy or its transfer.



System and surroundings: **system** – the part of the world in which we have a special interest. **Surroundings** – where we make observations, so huge they have either constant volume or constant pressure regardless of any changes in the system. The surroundings remain effectively the same size.

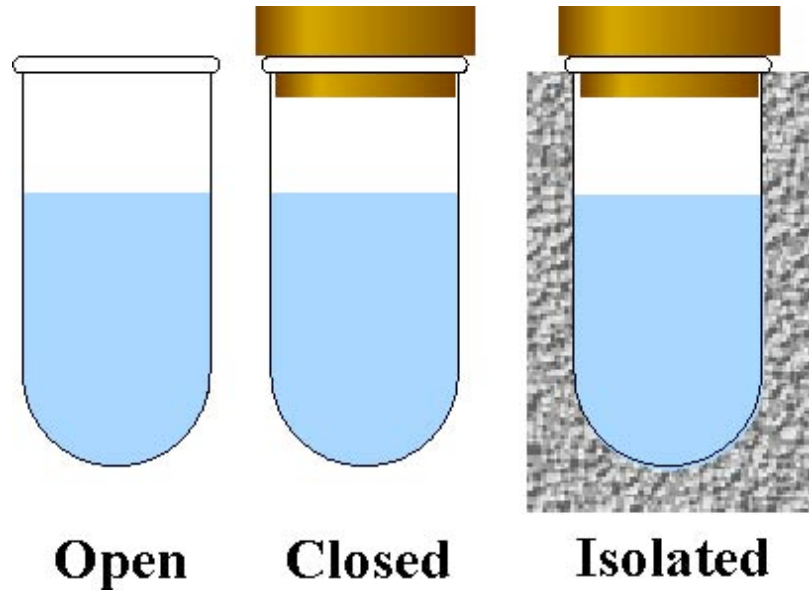
System and surroundings

Three types of system:

An **open system** – can exchange both energy and matter with its surroundings. (A flask that is not stoppered).

A **closed system** – can exchange energy but not matter with its surroundings. (A stoppered flask).

An **isolated system** – can exchange neither energy nor matter with its surroundings. (A sealed flask that is thermally, mechanically, and electrically insulated from its surroundings).



Work and heat

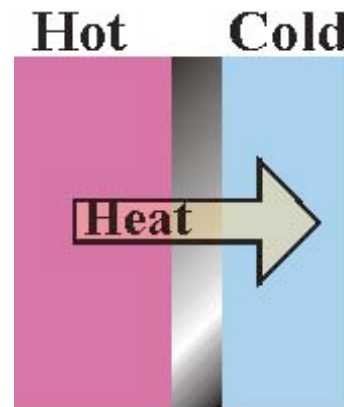
Energy can be exchanged between a closed system and its surroundings as work or as heat.

Work – a transfer of energy that can cause motion against an opposing force. A process produces work if it can be used to change the height of a weight somewhere in the surroundings.

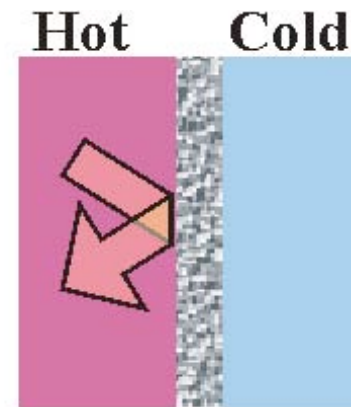
Heat – a transfer of energy as a result of a temperature difference between the system and its surroundings.

Walls that permit the passage of energy as heat – **diathermic**. (metal container).

Walls that do not permit heat to pass through though there is a difference in temperature – **adiabatic**. (vacuum flask).

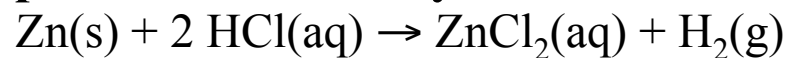


(a) Diathermic



(b) Adiabatic

Example of different ways to transfer energy:

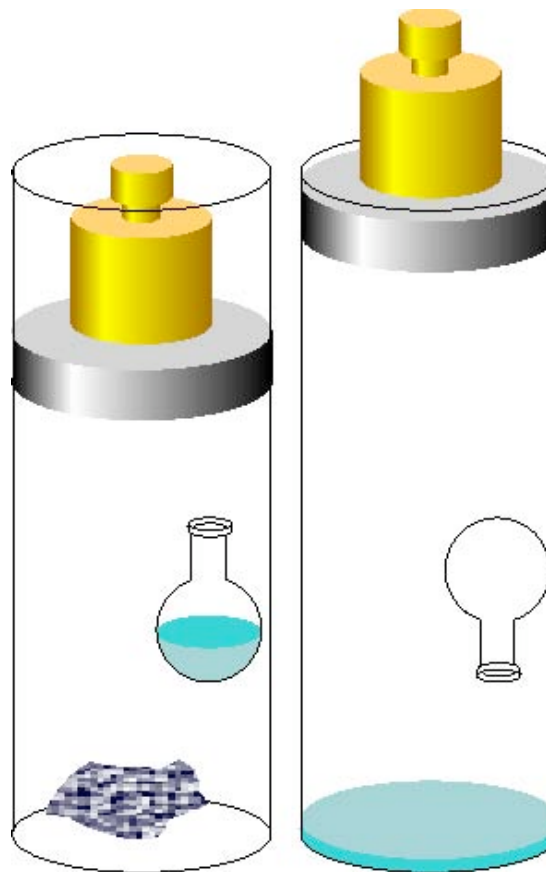


1. The reaction takes place inside a cylinder fitted with a piston – then the gas produced drives out the piston and raises its weight in the surroundings. Energy has migrated to the surroundings as a work. Some energy also migrates as heat – if the reaction vessel is in ice, some amount of ice melts.

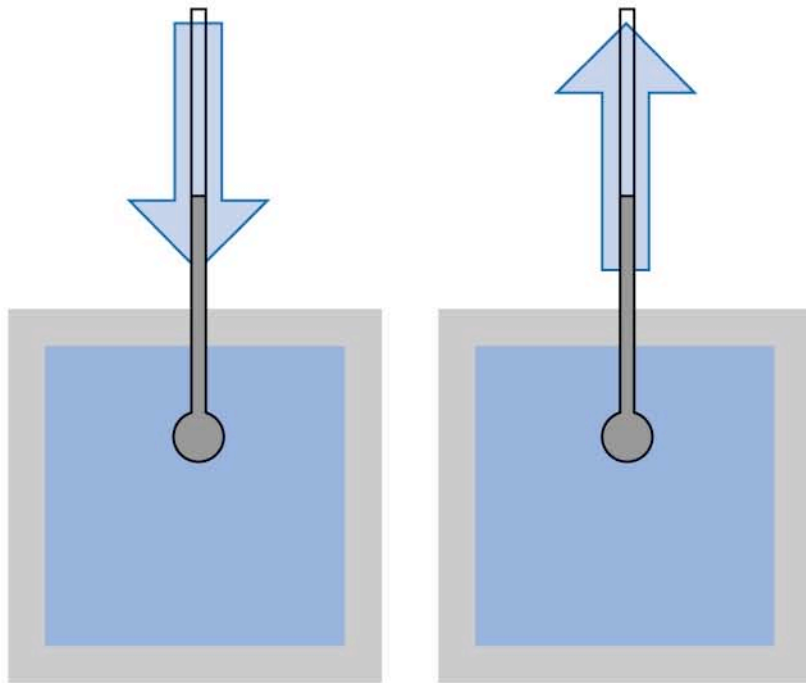
2. A piston is locked in position. No work is done. More ice melts – more energy has migrated to the surroundings as heat.

A process that releases heat into surroundings – **exothermic**.
(Combustion).

A process that absorbs energy from the surroundings – **endothermic**.
(Dissolution of ammonium nitrate in water).

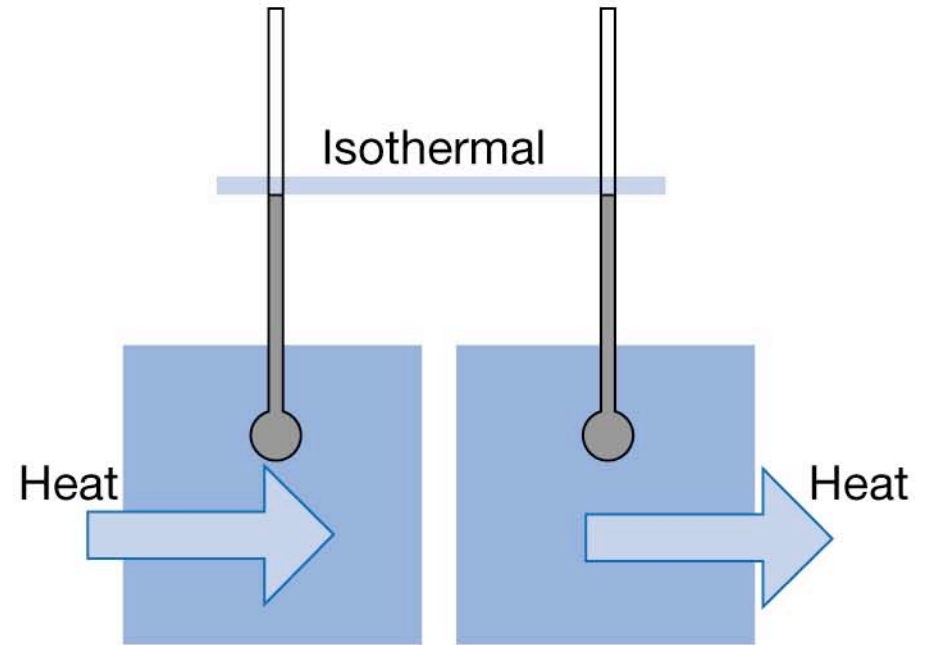


- (a) When an endothermic process occurs in an adiabatic system, the temperature falls;
- (b) If the process is exothermic, then the temperature rises;
- (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature;
- (d) If the process is exothermic, then energy leaves as heat and the process is isothermal.



(a)

(b)



(c)

(d)

Molecular nature of work

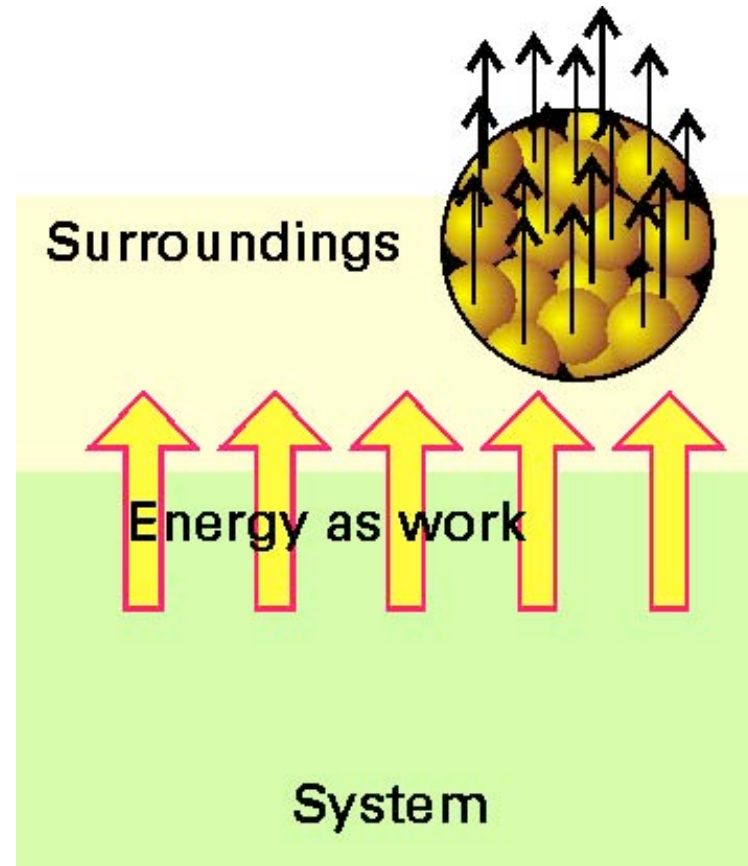
When a weight is raised, all its atoms move in the same direction.

Work is the transfer of energy that achieves or utilizes uniform motion in the surroundings.

Whenever we think of work, we can always think of it in terms of uniform motion of some kind.

Electrical work – electrons are pushed in the same direction through the circuit.

Mechanical work – atoms are pushed in the same direction against an opposing force.

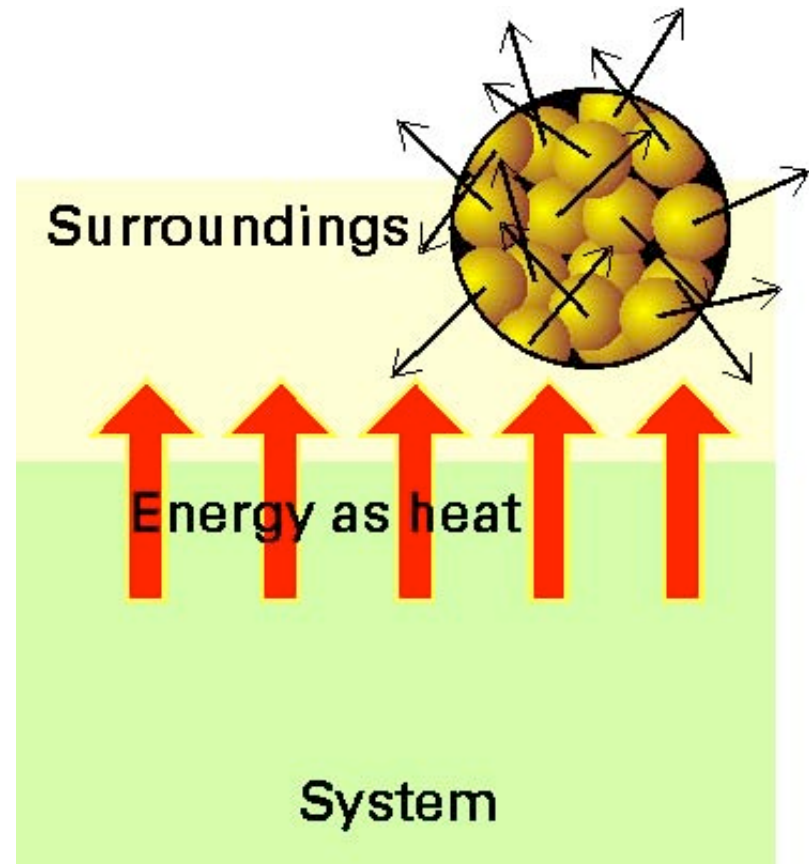


Molecular nature of heat

The motion stimulated by the arrival of energy from the system is disorderly, not uniform as in the case of work.

Heat is the transfer of energy that achieves or utilizes disorderly motion in the surroundings.

Fuel burning – generates disorderly molecular motion in its vicinity.



The First Law

The total energy of a system – **internal energy**, U : the total kinetic and potential energy of the molecules in the system. The change in internal energy:

$$\Delta U = U_f - U_i$$

U_f – internal energy at a final state

U_i – internal energy at an initial state

The internal energy is a **state function**: its value depends only on the current state of the system and is independent on how this state was prepared. It is a function of properties that determine the physical state of the system, i.e., pressure, volume, temperature, and amount of substance. Changing any of these variables changes U . The internal energy is an extensive property – it depends on the amount of substance. The **molar internal energy**, $U_m = U/n$ – intensive property, does not depend on the amount of substance, but depends on the temperature and pressure.

Internal energy, heat, and work are all measured in the same units, the joule (J):

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

Changes in molar internal energy ΔU_m are typically expressed in kilojoules per mole (kJ mol^{-1}).

An energy of 1 cal is enough to raise the temperature of 1 g of water by 1°C :

$$1 \text{ cal} = 4.184 \text{ J}$$

Molecular interpretation: The internal energy of gas

A 'quadratic contribution' to the energy – a contribution that can be expressed as the square of a variable, such as the position or the velocity. The kinetic energy of a moving atom:

$$E_K = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

The **equipartition theorem**: for a collection of particles at thermal equilibrium at a temperature T , *the average value of each quadratic contribution to the energy is the same and equal to $(1/2)kT$.* k – Boltzmann's constant.

The equipartition theorem is a conclusion from classical mechanics. In practice, it can be used for molecular translation and rotation but not vibration.

If we consider the moving atom, according to the equipartition theorem, the average energy of each term in the expression for kinetic energy is $(1/2)kT$. Therefore, the mean energy of the atom is $(3/2)kT$ and the total energy of the gas (without potential energy contribution) is $(3/2)NkT = (3/2)nRT$.

$$U_m = U_m(0) + \frac{3}{2}RT$$

U_m – the molar internal energy at $T = 0$, when all translational motion ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. We can see that the internal energy of a perfect gas increases linearly with temperature. At 25°C , $(3/2)RT = 3.7 \text{ kJ mol}^{-1}$.

Because the potential energy of interactions between the atoms or molecules of a perfect gas is zero, the internal energy is independent of how close they are together, i.e., of volume: $\left(\frac{\partial U}{\partial V}\right)_T = 0$. The internal energy of interacting molecules in addition has a contribution from the potential energy. However, no simple expressions can be written down in general. Nevertheless, as a temperature of a system is raised, the internal energy increases as the various modes of motion become more highly excited.

The conservation of energy

Experimental finding: the internal energy of a system may be changed either by doing work on the system or by heating it.

Heat and work are equivalent ways of changing a system's internal energy.

It is also found experimentally that, if a system is isolated from the surroundings, then no change in internal energy takes place.

Suppose we consider an isolated system. It can neither do work nor supply heat – the internal energy cannot change.

First Law of thermodynamics:

The internal energy of an isolated system is constant.

Impossibility of making a ‘perpetual motion machine’. No device has ever been made that creates internal energy to replace the energy drawn out as work. We cannot extract energy as work, leave the system isolated for some time, and hope when we return the internal energy will be restored to its original value.

The mathematical statement of the First Law:

w – the work done on the system

q – the energy transferred as heat to the system

$$\Delta U = w + q$$

The internal energy is constant in an isolated system ($q = 0$ and $w = 0$). The change of internal energy of a closed system is equal to the energy through its boundary as heat or work. ‘Acquisitive convention’: $w > 0$, $q > 0$ if the energy is transferred to the system as work or heat; $w < 0$, $q < 0$ if the energy is lost from the system as work or heat. We view the flow of energy as work or heat from the system’s perspective.

If we switch to infinitesimal changes, dU , dw , and dq ,

$$dU = dw + dq$$

The measurement of work

Work = distance \times opposing force

The work needed to raise the mass through a height h on the surface of Earth:

$$\text{Work} = h \times mg = mgh$$

$$\text{Work} = 1.0 \text{ kg} \times 9.81 \text{ m s}^{-2} \times 0.75 \text{ m} = 7.4 \text{ kg m}^2 \text{ s}^{-2} \quad 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

When energy *leaves* the system, i.e., the system does work in the surroundings, $w < 0$.

$$w = -100 \text{ J}$$

When energy *enters* the system as work, $w > 0$.

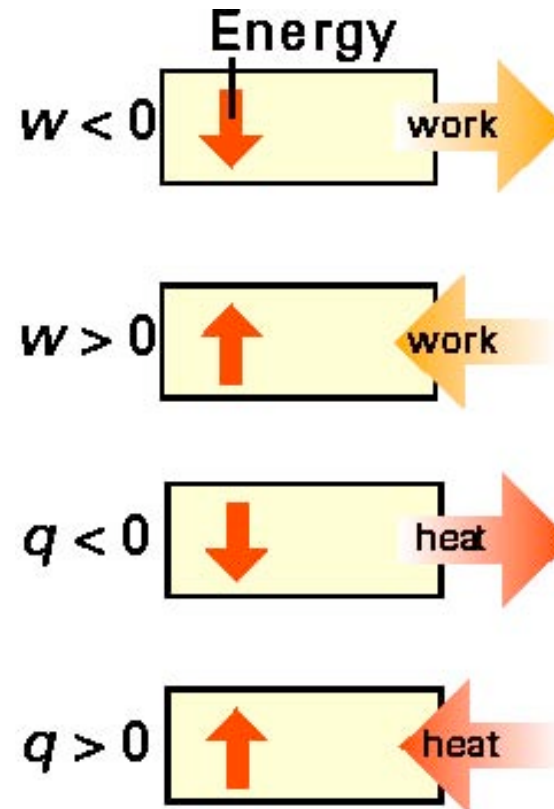
$$w = +100 \text{ J}$$

Energy leaves the system as heat, $q < 0$.

$$q = -100 \text{ J}$$

Energy enters the system as heat, $q > 0$.

$$q = +100 \text{ J}$$



Expansion work

The work arising from a change in volume; includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation or consumption of gases.

The general expression for work

$$dw = -F dz$$

The negative sign: when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease.

$$F = p_{\text{ex}} A \quad dw = -p_{\text{ex}} A dz \quad dV = A dz$$

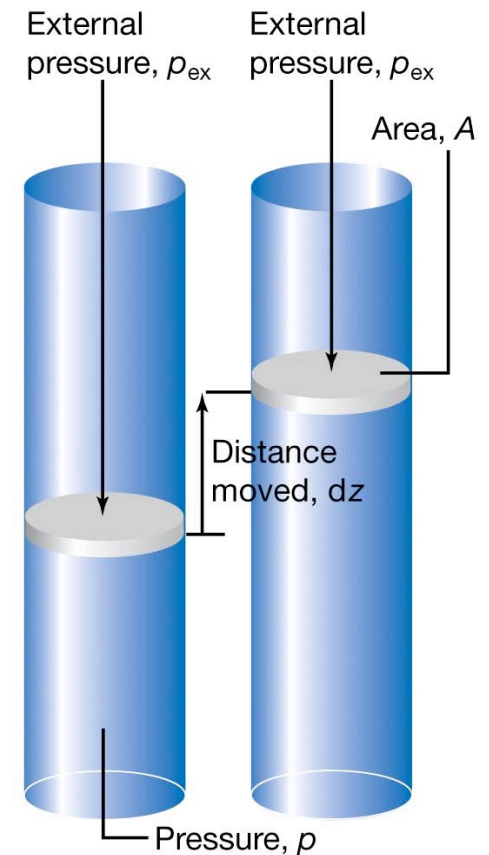
$$dw = -p_{\text{ex}} dV$$

$$w = -\int_{V_i}^{V_f} p_{\text{ex}} dV$$

Free expansion

Expansion against zero opposing force: $p_{\text{ex}} = 0 \quad w = 0$

No work is done when a system expands freely. Expansion of this kind occurs when a system expands into a vacuum.



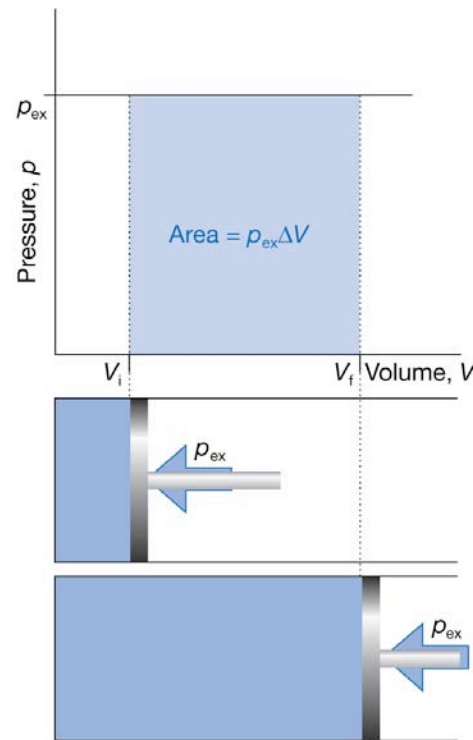
Expansion against constant pressure

Suppose that the external pressure is constant throughout the expansion. The piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example: the expansion of a gas formed in a chemical reaction.

$$w = - \int_{V_i}^{V_f} p_{ex} dV = -p_{ex} (V_f - V_i)$$

$$\Delta V = V_f - V_i \quad w = -p_{ex} \Delta V$$

The value of the integral $\int_a^b f(x)dx$ is equal to the area under the graph of $f(x)$ between $x = a$ and $x = b$.



Reversible expansion

A **reversible change** - a change that can be reversed by infinitesimal modification of a variable. We say that a system is in **equilibrium** with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state. Suppose a gas is confined by a piston and that the external pressure, p_{ex} , is set to be equal to the pressure, p , of the confined gas. Such system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions. To achieve reversible expansion p_{ex} should be equal p at each stage.

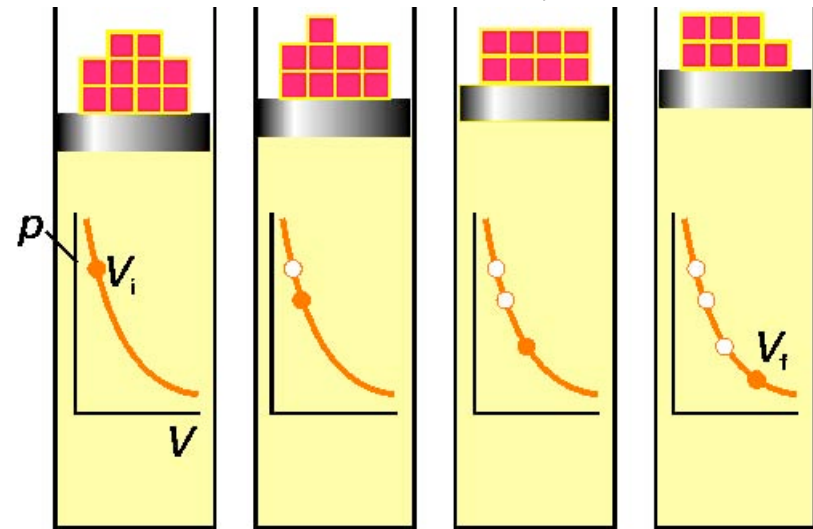
$$dw = -p_{ex} dV \quad dw = -pdV \quad w = - \int_{V_i}^{V_f} pdV$$

$$p = \frac{nRT}{V} \quad w = - \int_{V_i}^{V_f} pdV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

Reversible isothermal expansion work of a perfect gas at a temperature T

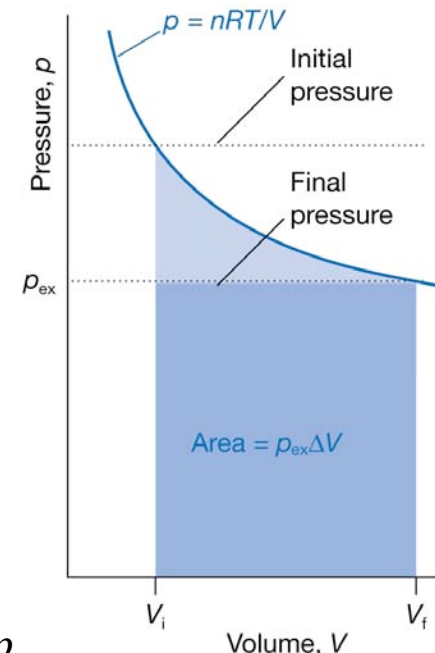
For a gas to expand reversibly, the external pressure must be adjusted to match the internal pressure at each stage of the expansion. This matching is represented in this illustration by gradually unloading weights from the piston as the piston is raised and the internal pressure falls. The procedure results in the extraction of the maximum possible work of isothermal expansion.

$$w = -nRT \ln \frac{V_f}{V_i}$$



1. A system does maximum expansion work when the external pressure is equal to that of the system ($p_{\text{ex}} = p$).
2. A system does maximum expansion work when it is in mechanical equilibrium with its surroundings.
3. Maximum expansion work is achieved in a reversible change.

More work is obtained when the expansion is reversible because matching the external pressure to the internal pressure at each stage of the process ensures that none of the system's pushing power is wasted. We cannot obtain more work than for the reversible process because increasing external pressure even infinitesimally at any stage results in compression. Also, some pushing power is wasted when $p > p_{\text{ex}}$.

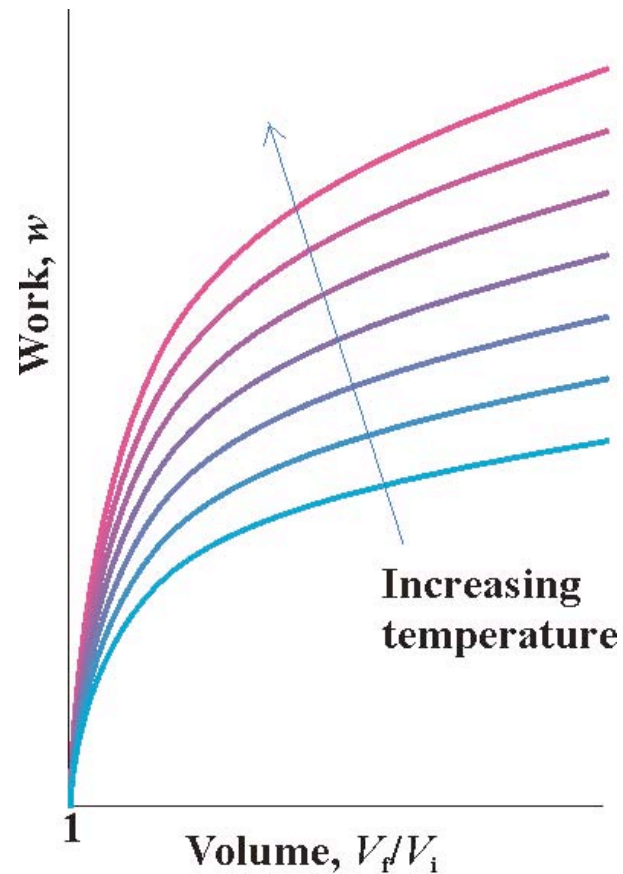


$$w = -nRT \ln \frac{V_f}{V_i}$$

In an expansion $V_f > V_i$, $V_f/V_i > 1$ – the logarithm is positive and $w < 0$.

Energy *leaves* the system as the system does expansion work.

For a given change in volume, we get more work the higher the temperature of the confined gas. At high temperatures, the pressure of gas is high, so we have to use a high external pressure, and therefore a stronger opposing force, to match the internal pressure at each stage.



Method for measuring the change in internal energy

By measuring the energy supplied to a constant-volume system as heat ($q > 0$) or obtained from it as heat ($q < 0$), we are in fact measuring the change in its internal energy.

The measurement of heat

The supply of heat to a system results in a rise of temperature, so one way to measure the value of q is to use a **calorimeter**. A calorimeter includes: a container, a thermometer, a surrounding water bath. The entire assembly is insulated from the rest of the world. To measure a change in internal energy, we should use a calorimeter that has a fixed volume and monitor the heat released ($q < 0$) or supplied ($q > 0$).

Bomb calorimeter

To ensure that no heat escapes unnoticed from the calorimeter it is immersed in a water bath with a temperature adjusted to match the the rising temperature of the calorimeter. The temperature of the bath is the same as that of the calorimeter – no heat flows from one to the other – adiabatic arrangement.

1. Calibration of a calorimeter – the observed change in temperature is compared with a change in temperature brought by a known quantity of heat.

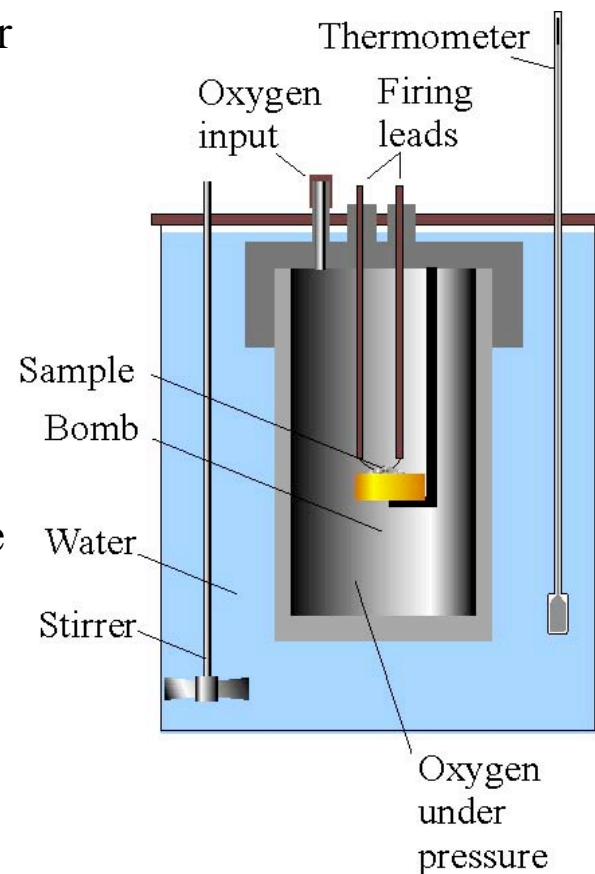
Electric heating for a measured time: $q = IVt$

Heat capacity, C , of the calorimeter

Heat capacity = (heat supplied)/(temperature rise), $C = q/\Delta T$

Using a reaction of known heat output – combustion of benzoic acid.

2. The heat capacity is used to interpret a temperature rise in a combustion experiment in terms of the heat released by the reaction.



Example 1. Calculating the work of gas production

Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce hydrogen gas in (a) a closed vessel of a fixed volume, (b) an open beaker at 25°C.

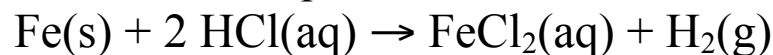
In (a) the volume cannot change, no expansion work is done and $w = 0$. In (b) the gas drives back the atmosphere and therefore $w = -p_{\text{ex}}\Delta V$. We can neglect the initial volume because the final volume after the gas production is so much larger:

$$\Delta V = V_f - V_i \approx V_f = nRT/p_{\text{ex}}$$

n – the amount of H₂ produced

$$w = -p_{\text{ex}}\Delta V = -p_{\text{ex}} \times (nRT/p_{\text{ex}}) = -nRT$$

The reaction equation is



Therefore, 1 mol H₂ is generated when 1 mol Fe is consumed and n can be taken as the amount of reacting Fe atoms.

$$M_{\text{Fe}} = 55.85 \text{ g mol}^{-1} \quad n_{\text{Fe}} = 50 \text{ g} / 55.85 \text{ g mol}^{-1}$$

$$w \approx -(50 \text{ g} / 55.85 \text{ g mol}^{-1}) \times 8.31451 \text{ J K mol}^{-1} \times 298.15 \text{ K} \approx -2.2 \text{ kJ}$$

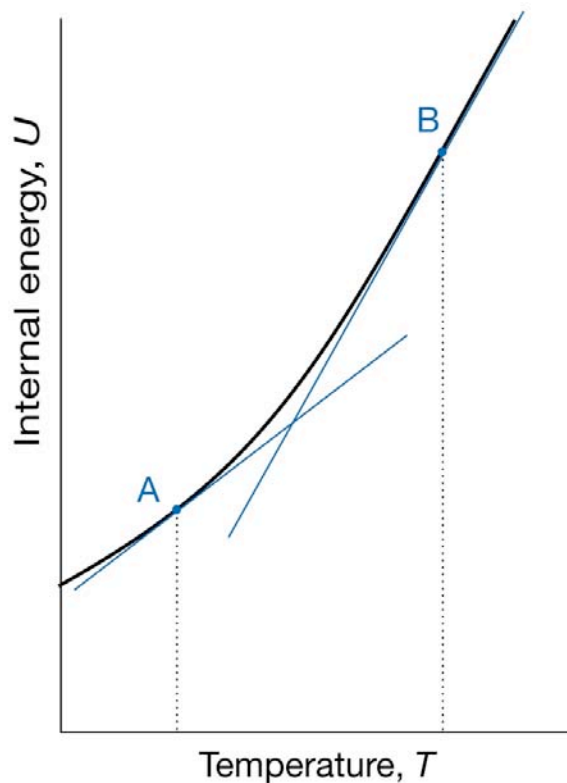
The reaction mixture does 2.2 kJ of work driving back the atmosphere. Note that for this perfect gas system the external pressure does not affect the final result: the lower the pressure, the larger the volume occupied by the gas, so the effects cancel.

Heat capacity

The internal energy of a substance increases when its temperature is raised. Let's suppose that the sample is confined to a constant volume. If the internal energy is plotted against temperature, the slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** is denoted C_V and is defined formally as

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

A partial derivative is slope calculated with all variables except one held constant. In this case, the internal energy varies with the temperature and with the volume of the system, but we are interested only in its variation with the temperature, the volume being held constant.



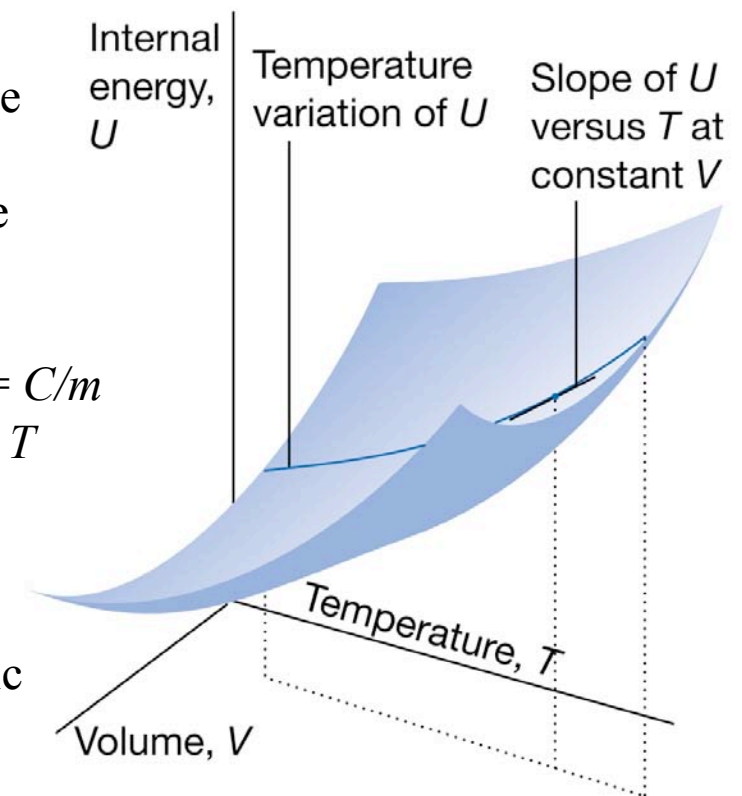
Heat capacity – an **extensive** property – depends on the size of the sample.

More convenient to report the heat capacity as an **intensive** property.

Specific heat capacity – $C_s = C/m$
 $\sim 4 \text{ J K}^{-1} \text{ g}^{-1}$ for water at room T

Molar heat capacity at constant volume –

$C_{V,m} = C_V/n$
 $\sim 25 \text{ J K}^{-1} \text{ mol}^{-1}$ for polyatomic gases



Heat transactions

The change of internal energy of a system:

$$dU = dq + dw_{\text{exp}} + dw_e$$

dw_e – extra work in addition to the expansion work dw_{exp}

At constant volume and no extra work:

$$dU = dq \quad \Delta U = q_V$$

The heat capacity of a monoatomic perfect gas can be calculated by taking the partial derivative of the expression for the internal energy:

$$U_m = U_m(0) + \frac{3}{2}RT \quad C_{V,m} = \frac{\partial}{\partial T} \left(U_m(0) + \frac{3}{2}RT \right) = \frac{3}{2}R$$

The numerical value is $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$.

The heat capacity can be used to relate a change in internal energy to a change in temperature of a constant-volume system:

$$dU = C_V dT \quad (\text{at constant volume})$$

If the heat capacity is independent of temperature over the range of temperatures of interest, then

$$\Delta U = C_V \Delta T \quad (\text{at constant volume})$$

Because a change in internal energy can be identified with the heat supplied at constant volume,

$$q_V = C_V \Delta T$$

A simple way of measuring the heat capacity of a sample: a measured quantity of heat is supplied to the sample (electrically, for example), and the resulting increase in temperature is monitored.

Then,

$$C_V = q_V / \Delta T$$

A large heat capacity: for a given quantity of heat, there will be only a small increase in temperature.

An infinite heat capacity: there will be no increase in temperature however much heat is supplied.

At a phase transition (the boiling point of water), the temperature of a substance does not rise as heat is supplied:

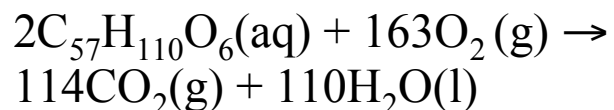
the energy is used to drive the endothermic phase transition (to vaporize the water), rather than to increase its temperature.

Therefore, at the temperature of a phase transition, the heat capacity of a sample is infinite.

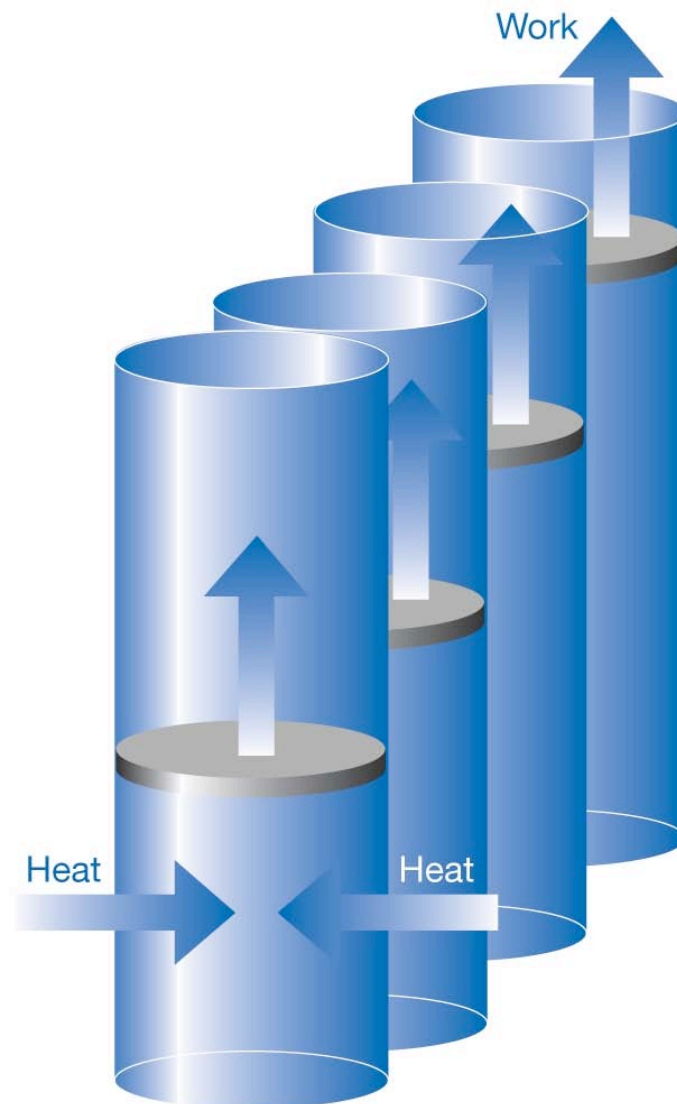
The enthalpy

Much of chemistry and most of biology takes place in vessels that are open to the atmosphere and subjected to constant pressure, not maintained at constant volume – the volume of the system changes.

Oxidation of a fat:



Net decrease in volume, elimination of $(163-114) = 49$ mol gas molecules. The atmosphere does work on the system as the reaction proceeds – the energy is transferred as work from the surroundings – decrease in the internal energy is less than the energy released as heat because some energy has been restored as work. To avoid this complication, we introduce ‘enthalpy’.



The definition of enthalpy

The **enthalpy** (*heat inside*), H , of a system is defined as

$$H = U + pV$$

The enthalpy of a system is always greater than its internal energy.

Enthalpy – extensive property.

Molar enthalpy, $H_m = H/n$

$$H_m = U_m + pV_m$$

For a perfect gas, $H_m = U_m + RT$

The difference between the molar enthalpy and molar internal energy of a perfect gas increases with temperature. At 25°C, $RT = 2.5 \text{ kJ mol}^{-1}$. Because the molar volume of a solid or liquid is typically ~1000 times less than that of gas, the molar enthalpy of a solid or liquid is only ~2.5 J mol⁻¹ more than its molar internal energy, so the numerical difference is negligible.

H is defined in terms of state functions (U , p , and V) – *the enthalpy is a state function*. The change in enthalpy ΔH , when a system changes from one state to another is independent of the path between two states.

Heat transfer at constant pressure

At constant pressure: $\Delta H = q_p$. At constant pressure we can identify the heat transferred with a change in enthalpy of the system.

For a general infinitesimal change of state of the system,

U changes to $U + dU$, p to $p + dp$, V to $V + dV$:

$H + dH = (U + dU) + (p + dp)(V + dV) = U + dU + pV + pdV + Vdp + dpdV$
 $dpdV$ – the product of two infinitesimally small numbers and can be ignored.

$$U + pV = H$$

$$H + dH = H + dU + pdV + Vdp$$

$$dH = dU + pdV + Vdp$$

$$dU = dq + dw$$

$$dH = dq + dw + pdV + Vdp$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work,

$$dw = -pdV$$

$$dH = dq + Vdp$$

The heating occurs at constant pressure:

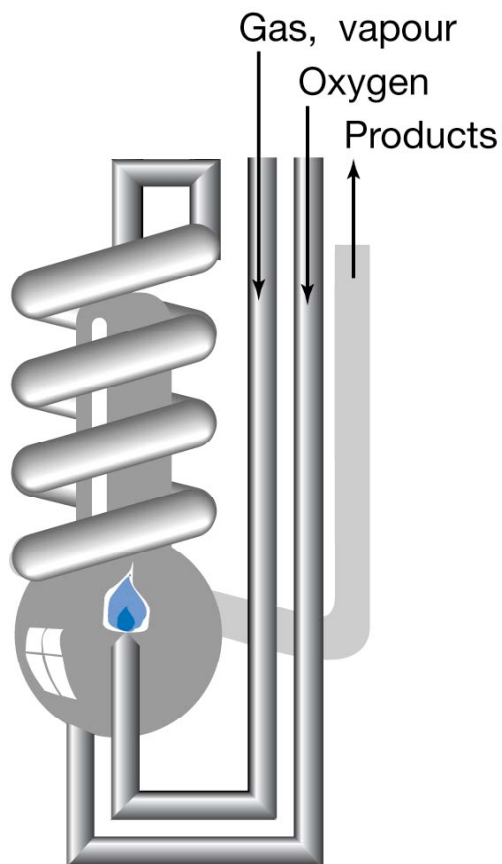
$$dp = 0$$

$$dH = dq$$

When a system is subjected to a constant pressure, and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat.

The measurement of an enthalpy change

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change at constant pressure: **isobaric calorimeter**.



A thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature. For a combustion reaction an **adiabatic flame calorimeter** may be used to measure ΔT when a given amount of substance burns in a supply of oxygen. Another route: to measure ΔU using a bomb calorimeter, and then convert ΔU to ΔH . Because solids and liquids have small molar volumes, for them pV_m is so small that the molar enthalpy and molar internal energy are almost identical:

$$H_m = U_m + pV_m \approx U_m$$

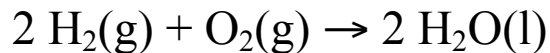
If a process involves only solids or liquids, the values of ΔU and ΔH are almost identical. But this is not the case when gases are produced or consumed in the reaction.

The enthalpy of a perfect gas: $H = U + pV = U + nRT$

The change of enthalpy in a reaction that produces or consumes gas:

$$\Delta H = \Delta U + \Delta n_g RT$$

Δn_g – the change of the amount of gas molecules in the reaction.



3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules:

$$\Delta n_g = -3 \quad \text{At } 298 \text{ K} \quad \Delta H - \Delta U = -3RT \approx -7.4 \text{ kJ}$$

Example 2. Relating ΔH and ΔU

The internal energy change when 1.0 mol CaCO_3 in the form of calcite converts to aragonite is +0.21 kJ. Calculate the difference between the enthalpy change and the change in internal energy when the pressure is 1.0 bar given that the densities of the solids are 2.71 and 2.93 g cm^{-3} .

We need to relate the density and the molar mass. For 1 mol,

$$\rho = M/V_m \quad V_m = M/\rho$$

The change in enthalpy when the transition occurs is

$$\Delta H = H(\text{aragonite}) - H(\text{calcite}) = \{U(\text{a}) + pV(\text{a})\} - \{U(\text{c}) + pV(\text{c})\} = \Delta U + p\{V(\text{a}) - V(\text{c})\} = \Delta U + p\Delta V$$

$$V_m(\text{a}) = 100 \text{ g} / 2.71 \text{ g cm}^{-3} = 37 \text{ cm}^3 \quad V_m(\text{c}) = 100 \text{ g} / 2.93 \text{ g cm}^{-3} = 34 \text{ cm}^3$$

$$p\Delta V = 1.0 \times 10^5 \text{ Pa} \times (37 - 34) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J} \quad \Delta H - \Delta U = -0.3 \text{ J}$$

The difference is only 0.1% of the value of ΔU .

Example 3. Calculating a change in enthalpy

Water is heated under $p = 1$ atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s, 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

$$\Delta H = q_p = IVt$$

$$\Delta H_m = 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s} / (0.798/18.02) \text{ mol}$$

$$\Delta H_m = +41 \text{ kJ mol}^{-1} \quad \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)} \quad \Delta n_g = +1 \text{ mol}$$

$$\Delta U_m = \Delta H_m - RT = +38 \text{ kJ mol}^{-1}$$

The variation of the enthalpy with temperature

The enthalpy of a substance increases with temperature. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (constant pressure or constant volume). The most important condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**, C_p .

The heat capacity at constant - the analog of the heat capacity at constant volume, an extensive property. The **molar heat capacity at constant pressure**, $C_{p,m}$, - an intensive property.

$$dH = C_p dT \quad (\text{at constant pressure})$$

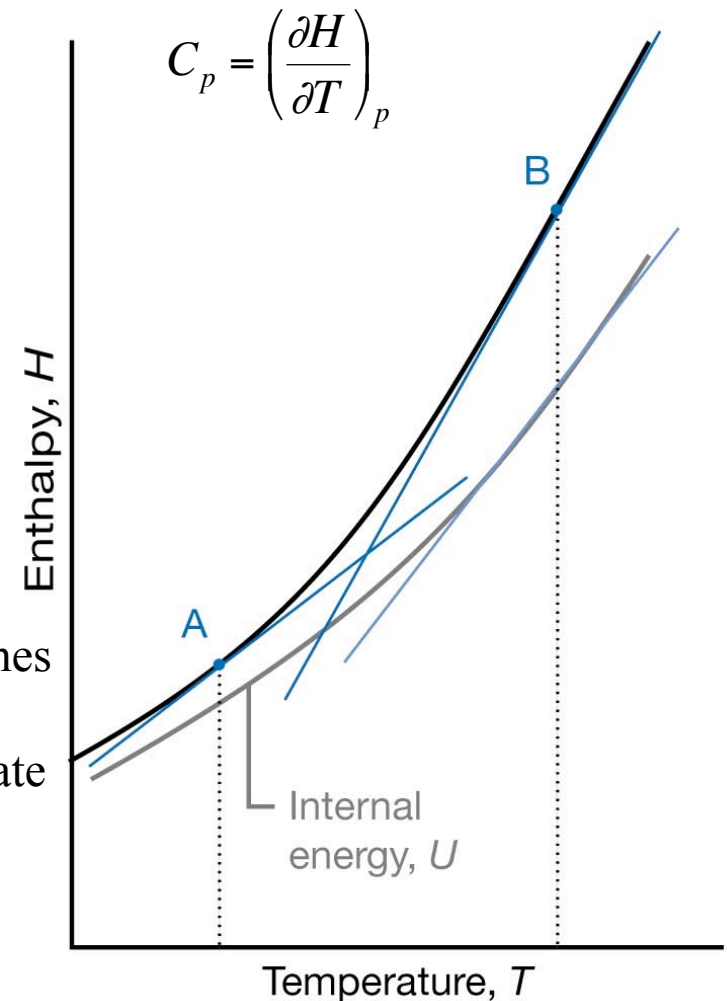
$$\Delta H = C_p \Delta T \quad (\text{at constant pressure}) \quad q_p = C_p \Delta T$$

How to measure the heat capacity of a capacity of a sample: a measured quantity of heat is supplied under constant pressure (as in a sample exposed to the atmosphere and free to expand), and the temperature rise is monitored.

The variation of heat capacity with temperature can sometimes be ignored if the temperature range is small - accurate for a monoatomic perfect gas. Otherwise, a convenient approximate empirical expression is

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

The empirical parameters a , b , and c are independent of temperature.



Example 4. Evaluating an increase in enthalpy with temperature

What is the change in molar enthalpy of N₂ when it is heated from 25°C to 100°C?

For N₂(g) we find in Table 2.2 $a = 28.58 \text{ J K}^{-1} \text{ mol}^{-1}$, $b = 3.77 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$, and $c = -0.50 \times 10^5 \text{ J K mol}^{-1}$.

$$\text{Since } dH = C_p dT, \quad C_{p,m} = a + bT + \frac{c}{T^2}$$
$$\Delta H = H(T_2) - H(T_1) = \int_{H(T_1)}^{H(T_2)} dH = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) dT \quad T_1 = 298 \text{ K} \quad T_2 = 373 \text{ K}$$

To carry out the integration, we use

$$\int dx = x + \text{constant} \quad \int x dx = \frac{1}{2} x^2 + \text{constant} \quad \int \frac{dx}{x^2} = -\frac{1}{x} + \text{constant}$$

$$H(T_2) - H(T_1) = a(T_2 - T_1) + \frac{1}{2} b(T_2^2 - T_1^2) - c \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad H(373 \text{ K}) = H(298 \text{ K}) + 2.20 \text{ kJ mol}^{-1}$$

If we had assumed a constant heat capacity of 29.14 J K⁻¹ mol⁻¹ (the value given by the equation at 25°C), we would have found $\Delta H = 2.19 \text{ kJ mol}^{-1}$.

Interestingly, at very low temperatures the heat capacity of a solid is proportional to T^3 (**Debye T^3 law**), $C_p = aT^3$

If we calculate the change in enthalpy of such a substance when it is heated from 0 to a temperature T , we obtain $\Delta H = (1/4)aT^4$

The heat capacity at constant volume is the slope of a plot of internal energy against temperature.

The heat capacity at constant pressure is the slope of a plot of enthalpy against temperature.

The relation between heat capacities

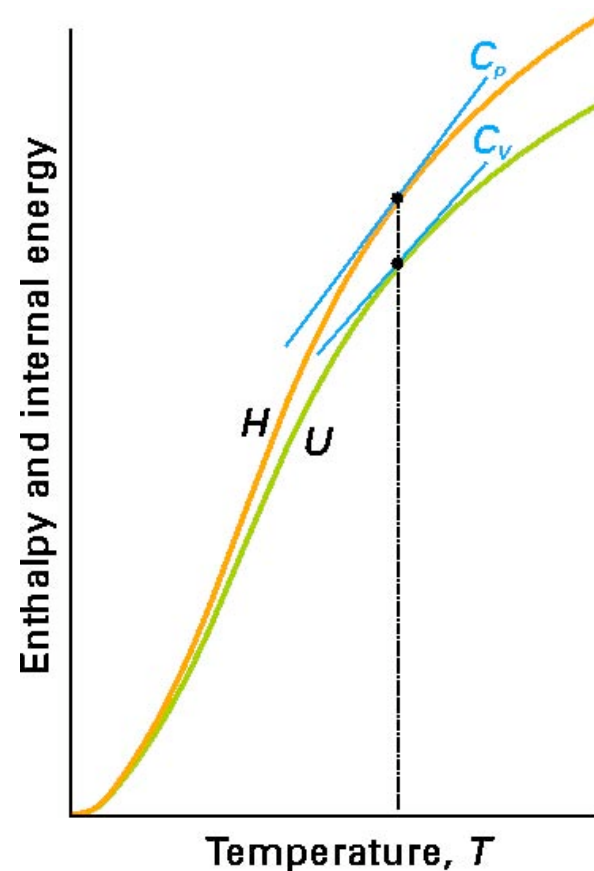
For a perfect gas, $H_m - U_m = RT$

$$\Delta H_m - \Delta U_m = R\Delta T$$

$$\Delta H_m / \Delta T - \Delta U_m / \Delta T = R$$

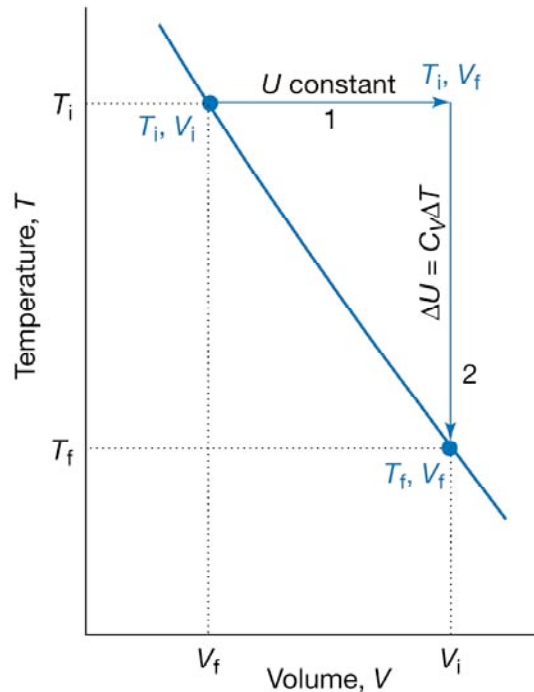
$$C_{p,m} - C_{v,m} = R$$

At constant volume, all the heat supplied to the system remains inside, and the temperature rises accordingly. At constant pressure, some of the energy supplied as heat escapes back into surroundings as work as the system expands. As less energy remains in the system, the temperature does not rise as much, which corresponds to a greater heat capacity.



$C_{p,m} - C_{v,m}$ – large for gases, but negligible for most solids and liquids.

Adiabatic change



The work of adiabatic change

The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as the sum of two steps. In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume, the overall change in internal energy arises solely from the second step, the change in temperature at constant volume.

Provided the heat capacity is independent of temperature,

$$\Delta U = C_V(T_f - T_i) = C_V\Delta T$$

The expansion is adiabatic $\Rightarrow q = 0$; because $\Delta U = q + w$, $\Delta U = w_{\text{ad}}$

The work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. On molecular grounds: the mean kinetic energy is proportional to T , so a change in internal energy arising from temperature alone is expected to be proportional to ΔT .

Now we need to relate the change in temperature to the change in volume (which is given). The most important type of adiabatic expansion is reversible adiabatic expansion, in which the external pressure is matched to the internal pressure throughout. For adiabatic reversible expansion we can derive

$$V_f T_f^c = V_i T_i^c \quad c = C_{V,m}/R$$

Derivation

Consider a stage in the expansion when the pressure inside and out is p :

$$dw = -pdV$$

For a perfect gas, $dU = C_V dT$ and $dU = dw + dq = dw$

Therefore, $C_V dT = -pdV$

We are dealing with a perfect gas and can replace p with nRT/V

$$\frac{C_V dT}{T} = -\frac{nR dV}{V} \quad C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} \quad \text{With } c = C_V/nR, \quad \ln \left(\frac{T_f}{T_i} \right)^c = \ln \left(\frac{V_i}{V_f} \right)$$

$$\text{Thus, } V_f T_f^c = V_i T_i^c \quad \text{and} \quad T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c}$$

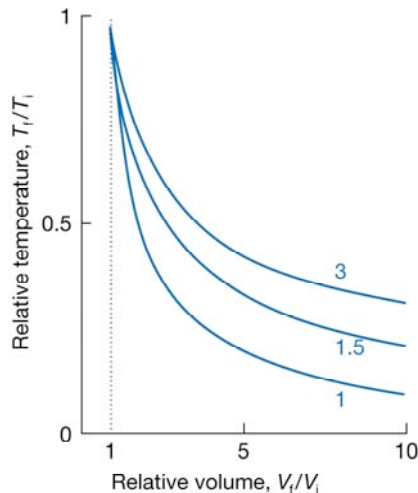
Consider the adiabatic reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 L to 1.00 L. The molar heat capacity of Ar at constant volume is 12.48 J K⁻¹ mol⁻¹, so $c = 1.501$.

$$T_f = (298 \text{ K}) \times (0.50 \text{ L} / 1.00 \text{ L})^{1/1.501} = 188 \text{ K}$$

$$\Delta T = -110 \text{ K}$$

$$w_{\text{ad}} = C_V \Delta T = 0.020 \text{ mol} \times 12.48 \text{ J K}^{-1} \text{ mol}^{-1} \times (-110 \text{ K}) = -27 \text{ J}$$

Note that temperature change is independent of the mass of gas but the work is not.



The variation of temperature as a perfect gas is expanded reversibly and adiabatically. The curves are labeled with different values of $c = C_{V,m}/R$. Note the temperature falls most steeply for gases with low molar heat capacity.

Heat capacity ratio and adiabats

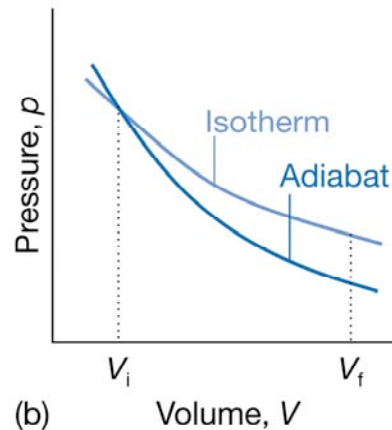
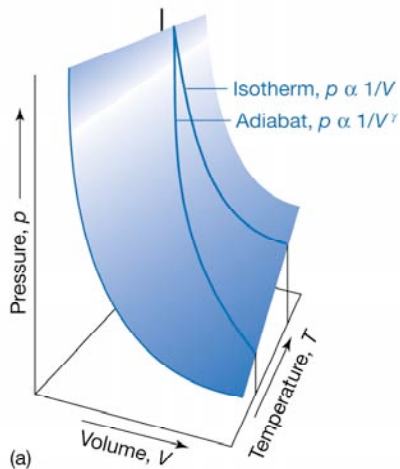
We consider the change in pressure resulting from an adiabatic, reversible expansion of a perfect gas. We will show $PV^\gamma = \text{constant}$ γ - the **heat capacity ratio**

$$\gamma = C_{p,m}/C_{V,m} \quad \text{Because } C_{p,m} > C_{V,m}, \gamma > 1 \quad \gamma = \frac{C_{V,m} + R}{C_{V,m}} = 1 + \frac{R}{C_{V,m}}$$

For a monoatomic perfect gas, $C_{V,m} = (3/2)R$, $\gamma = 5/3$. For a gas of non-linear polyatomic molecules (which can rotate as well as translate), $C_{V,m} = 3R$, $\gamma = 4/3$.

The initial and final states of a perfect gas satisfy the perfect gas law regardless how the change of state takes place:

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f} \quad \frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{1/c} = \left(\frac{V_f}{V_i}\right)^{\gamma-1} \quad (\gamma = 1 + 1/c) \quad \text{Then, } p_i V_i^\gamma = p_f V_f^\gamma$$



The curves of pressure vs. volume for adiabatic change – **adiabats**. Because $\gamma > 1$, an adiabat falls more steeply ($p \propto 1/V^\gamma$) than the corresponding isotherm ($p \propto 1/V$). The physical reason – in an isothermal expansion, energy flows to the system as heat and maintains the temperature \Rightarrow the pressure does not fall as much.

Thermochemistry

The study of the heat produced or required by chemical reactions – **thermochemistry**. It is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and surroundings. We can use calorimetry to measure the heat produced or absorbed by a reaction, and can identify q with a change in internal energy (a constant-volume process) or a change of enthalpy (a constant-pressure process). Conversely, if we know the ΔU or ΔH for a reaction, we can predict the heat the reaction can produce.

$\Delta H < 0$ – exothermic process $\Delta H > 0$ – endothermic process (at constant pressure)

Standard enthalpy changes

The reaction enthalpy depends on the conditions – the states of the reactants and products, the pressure, and the temperature – under which the reaction takes place. It is convenient to report the data for a set of standard conditions at the chosen temperature.

*The **standard state** of a substance is the pure substance at exactly 1 bar.*

The physical state and, when appropriate, solid phase, needs to be specified – we can speak of the standard states of the solid, liquid, or vapor phases of a substance, which are the pure solid, the pure liquid, or the pure solid, respectively, at 1 bar in each case. The temperature is not a part of the definition of a standard state – it is possible to speak of the standard state of hydrogen gas at 100 K, 273.15 K, or any other temperature. Conventionally, the data are reported at 298.15 K (25°C).

Enthalpies of physical change

A **phase** – a specific state of matter that is uniform throughout in composition and physical state. The liquid and vapor states of water – two of its phases.

The term phase – more specific than ‘state of matter’ – substance can exist in more than one solid form, each of them being a solid phase: rhombic and monoclinic sulfur, graphite and diamond, eight forms of ice, etc.

The conversion of one phase of a substance to another phase – **phase transition**: vaporization (liquid→gas), a transition between solid phases (graphite→diamond). Most phase transitions – accompanied by a change of enthalpy – the rearrangement of atoms and molecules usually requires energy.

The vaporization of a liquid (liquid water → to water vapor) – an endothermic process – heat must be supplied to make the change. At a molecular level, molecules are being driven apart from the grip they exert on one another – this process requires energy.

The energy that must be supplied as heat at constant pressure per mole of molecules that are vaporized – the **enthalpy of vaporization** of the liquid, $\Delta_{\text{vap}}H$.

Thermochemical equation:



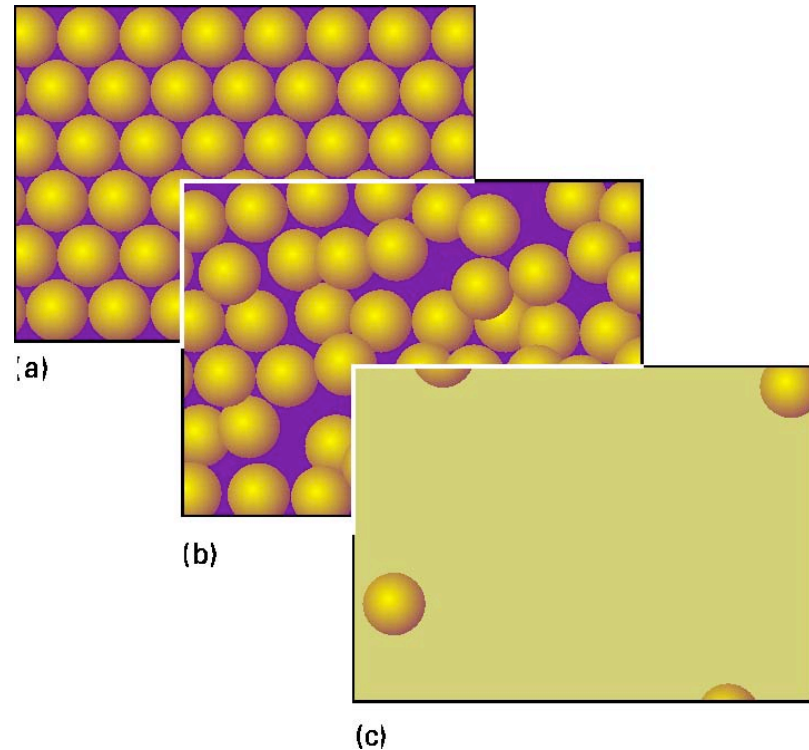
A thermochemical equation shows the enthalpy change (including the sign) that accompanies the conversion of an amount of reactant equal to its stoichiometric coefficient in the accompanying chemical equation.

Another common phase transition – **fusion**, or melting – when ice melts to water or iron becomes molten.

The enthalpy per mole of molecules – the **enthalpy of fusion**, $\Delta_{\text{fus}}H$. For water at 0°C – 6.01 kJ mol^{-1} – this amount of energy is needed to melt $1 \text{ mol H}_2\text{O(s)}$ at 0°C . All enthalpies of fusion are positive.

$\Delta_{\text{fus}}H$ of water is much smaller than $\Delta_{\text{vap}}H$. In vaporization, the molecules become completely separated from each other, whereas, when a solid melts, the molecules are merely loosened without separating completely.

When a solid (a) melts to a liquid (b), the molecules separate from one another only slightly, the intermolecular interactions are reduced only slightly, and there is only a small change of enthalpy. When a liquid vaporizes (c), the molecules are separated by a considerable distance, the intermolecular forces are reduced almost to zero, and the change in enthalpy is much greater.

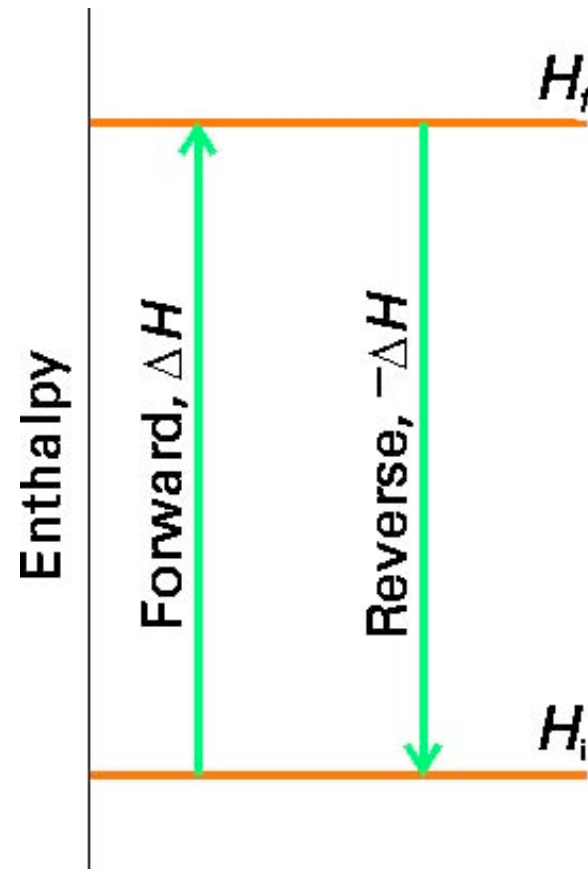


The reverse of vaporization – **condensation**, the reverse of fusion – **freezing**. The enthalpy change are, respectively, the negatives of the enthalpies of vaporization and fusion – the heat that is supplied to vaporize or melt the substance is released when it condenses or freezes.

The enthalpy change of a reverse transition is the negative of the enthalpy change of the forward transition (under the same conditions of temperature and pressure):



H is a state property, it must return to the same value if a forward change is followed by the reverse of that change. The high $\Delta_{\text{vap}}H$ of water (+44 kJ/mol) – a strongly endothermic process – implies that the condensation of water (- 44 kJ/mol) is a strongly exothermic process.



The direct conversion of a solid to a vapor – **sublimation**. The reverse process – **vapor deposition**.

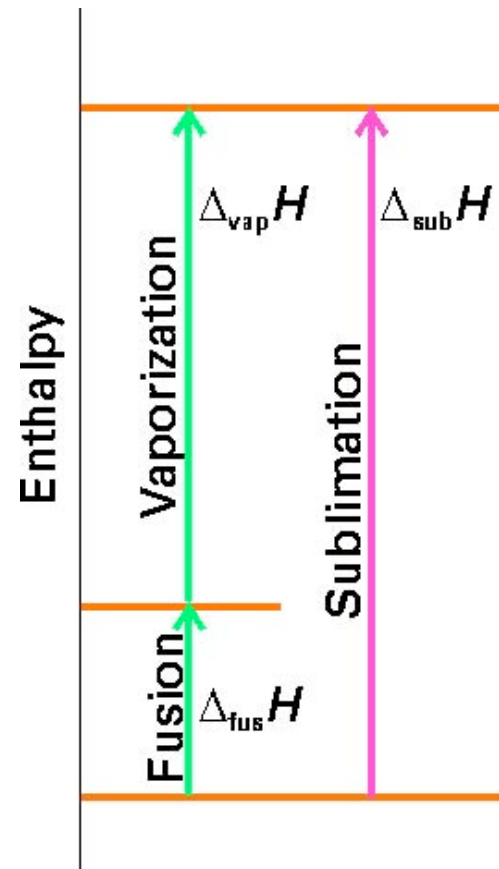
Frost vanishes as vapor without first melting on a cold, frosty morning. The vaporization of solid carbon dioxide (‘dry ice’).

The molar enthalpy change accompanying sublimation – the **enthalpy of sublimation**.

Because enthalpy is a state property, the same change in enthalpy must be obtained both in the *direct* conversion of solid to vapor and in the *indirect* conversion, in which solid first melts to liquid and then that liquid vaporizes.

$$\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H$$

The two enthalpies added must be for the same temperature. Adding together enthalpies of transitions for different temperatures gives a meaningless result.



Enthalpies of chemical change: Enthalpy changes accompanying chemical reactions:



During hydrogenation of ethane, the enthalpy of the system decreases by 137 kJ – if the reaction takes place at constant pressure, 137 kJ of heat is released into the surroundings when 1 mol $\text{CH}_2=\text{CH}_2$ combines with 1 mol H_2 at 25°C .

If we write ΔH^\ominus , we mean the change of enthalpy that occurs when the reactants in their standard states change into products in their standard states:

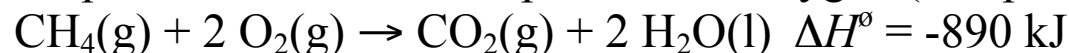
Pure, unmixed reactants \rightarrow pure, separated products (in their standard states)



When 2 mol H_2 as pure hydrogen gas at 1 bar combines with 1 mol O_2 as pure oxygen gas at 1 bar to form 2 mol H_2O as pure liquid water at 1 bar, the initial and final temperature being 25°C , the enthalpy of the system decreases by 572 kJ and (at constant p). 572 kJ of heat is released into the surroundings.

The **standard reaction enthalpy**, $\Delta_r H^\ominus$:
$$\Delta_r H^\ominus = \sum_{\text{products}} \nu H_m^\ominus - \sum_{\text{reactants}} \nu H_m^\ominus$$

Combustion – the complete reaction of a compound with oxygen (complete oxidation):



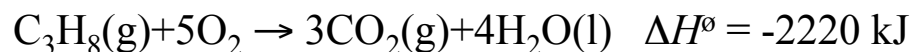
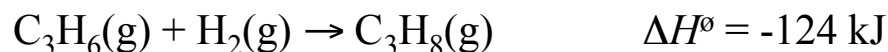
The **standard enthalpy of combustion**, $\Delta_c H^\ominus$ – the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is present. $\Delta_c H^\ominus$ – a molar quantity.

The combination of reaction enthalpies

Hess's law: *The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided.*

Consequence of enthalpy being a state function. The individual steps need not be actual reactions, they may be hypothetical. Their equations should balance and each step must correspond to the same temperature.

Given the thermochemical equations

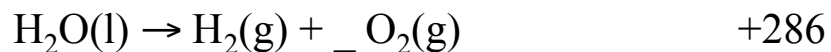
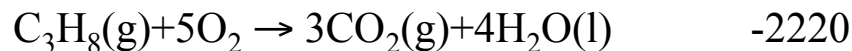
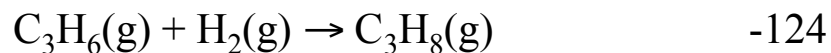


calculate the standard enthalpy of combustion of propene, C_3H_6 .

The overall reaction:



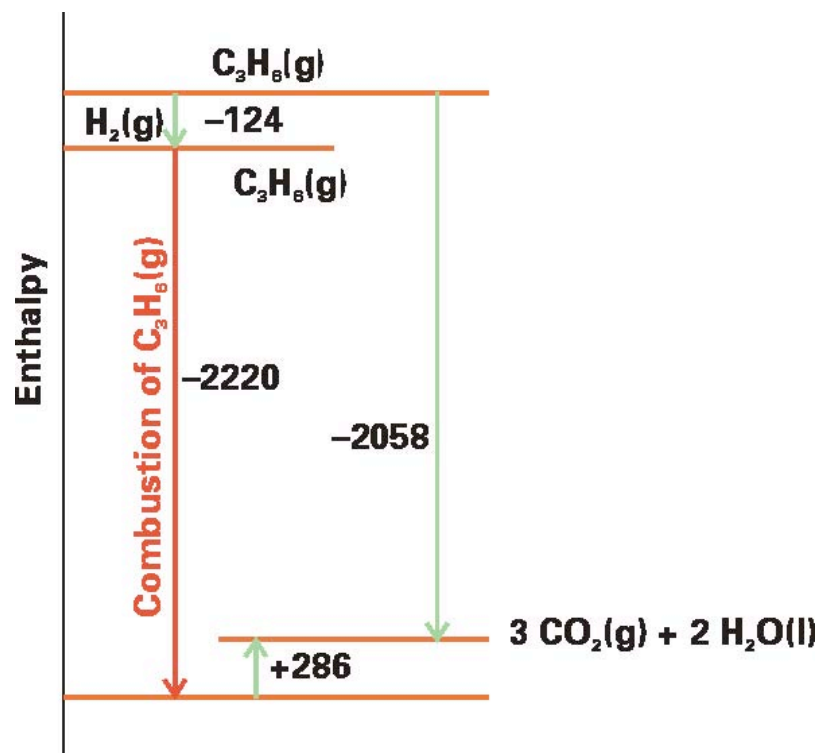
We recreate this equation from the following sum:
 $\Delta H^\circ/\text{kJ}$



Overall:



The standard enthalpy of combustion of propene: -2058 kJ mol⁻¹

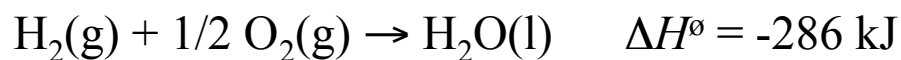


Standard enthalpies of formation

The **standard reaction enthalpy**, $\Delta_r H^\ominus$ – the difference between standard molar enthalpies of the reactants and the products, with each term weighted by the stoichiometric coefficient: $\Delta_r H^\ominus = \sum \nu H_m^\ominus(\text{products}) - \sum \nu H_m^\ominus(\text{reactants})$

The change of enthalpy of the system when the reactants in their standard state (pure, 1 bar) are completely converted into products in their standard states (pure, 1 bar). The problem – we have no way to know the absolute enthalpies of the substances. We can imagine that the reaction takes place by an indirect route – the reactants are first broken down into the elements and then products are formed from the elements.

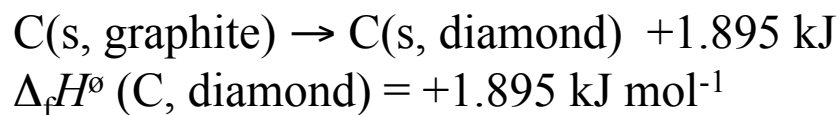
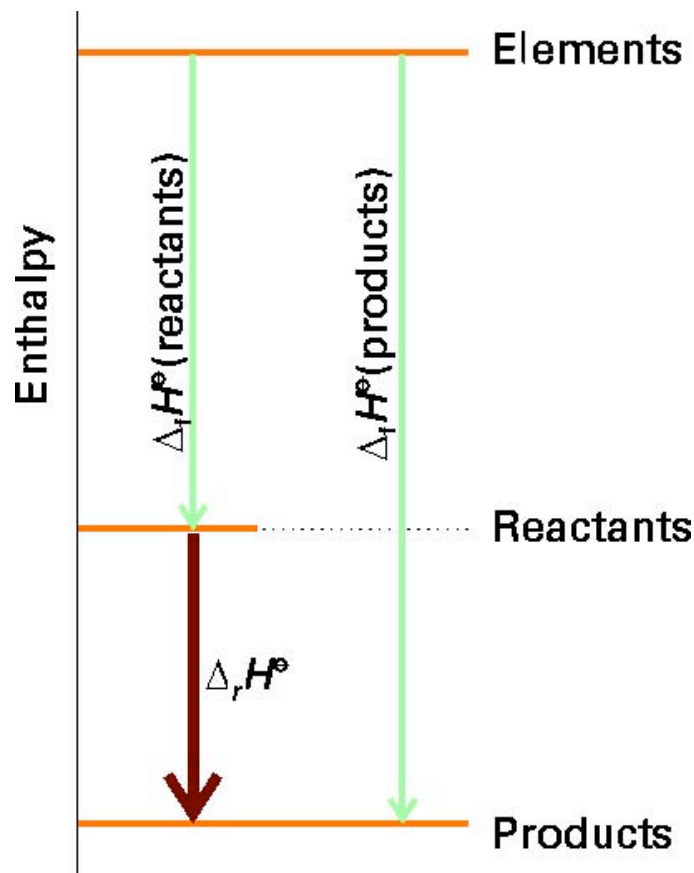
The **standard enthalpy of formation**, $\Delta_f H^\ominus$, of a substance – the standard enthalpy (per mole of the substance) for its formation from its elements in their reference states. The **reference state** of an element – its most stable form under prevailing conditions.



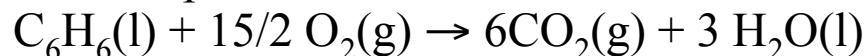
$$\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta_r H^\ominus = \sum \nu \Delta_f H^\ominus(\text{products}) - \sum \nu \Delta_f H^\ominus(\text{reactants})$$

The standard enthalpies of elements in their reference states are zero by definition.



Example: calculate the standard enthalpy of combustion of liquid benzene from the standard enthalpies of formation of the reactants and products.



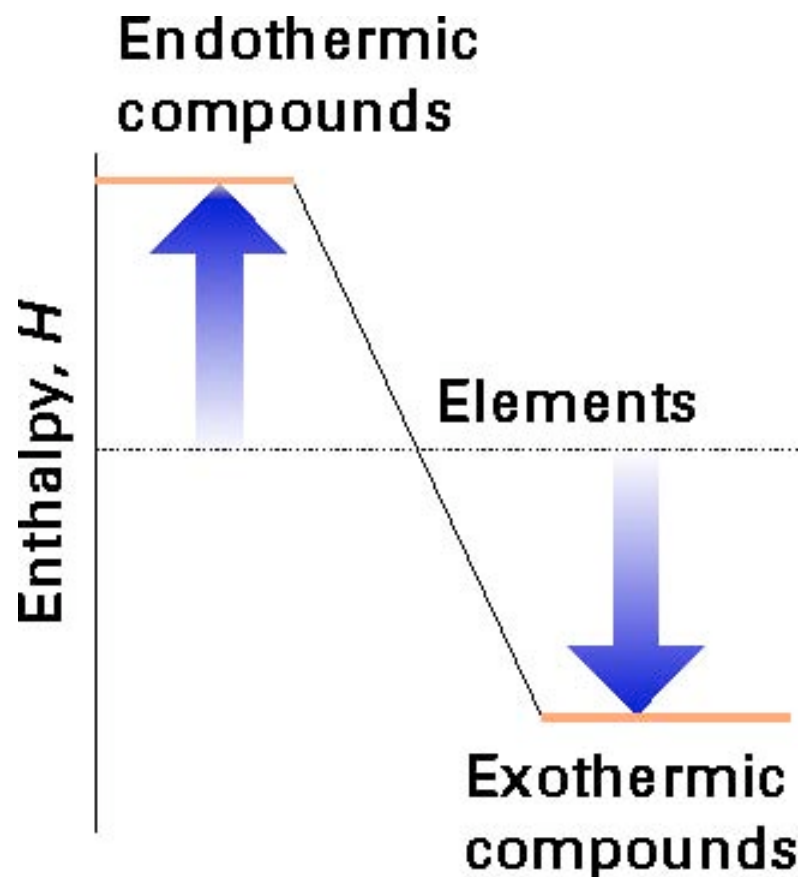
$$\Delta_r H^\ominus = \{6\Delta_f H^\ominus(\text{CO}_2, \text{g}) + 3\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l})\} - \{\Delta_f H^\ominus(\text{C}_6\text{H}_6, \text{l}) + 15/2\Delta_f H^\ominus(\text{O}_2, \text{g})\}$$

$$\Delta_r H^\ominus = \{6 \times (-395.15) + 3 \times (-285.83)\} - \{(49.0) + 15/2 \times (0)\} = -3268 \text{ kJ mol}^{-1}$$

The reference states of the elements define a thermochemical ‘sea level’, and enthalpies of formation can be regarded as thermochemical altitudes above or below sea level.

Compounds with negative standard enthalpies of formation – **exothermic compounds** – a lower enthalpy than their component elements.

Compounds with positive standard enthalpies of formation – **endothermic compounds** – a higher enthalpy than their component elements.



The temperature dependence of reaction enthalpies

Standard reaction enthalpies at different temperatures may be estimated from heat capacities and the reaction enthalpy at some other temperature.

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Because this equation applies to each substance in the reaction,

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT \quad \text{Kirchhoff's law}$$

$\Delta_r C_p^\ominus$ -the difference of the molar heat capacities of products and reactants weighted by their stoichiometric numbers from the chemical equation.

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$

When the heat capacity is independent of temperature, the integral in Kirchhoff's law evaluates to $(T_2 - T_1)\Delta_r C_p^\ominus$

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + (T_2 - T_1)\Delta_r C_p^\ominus$$

Example. The standard enthalpy of formation of gaseous H_2O at 298 K is $-241.82 \text{ kJ mol}^{-1}$. Estimate its value at 373 K given the following values of $C_{p,m}$: $\text{H}_2\text{O}(\text{g})$: $33.58 \text{ J K}^{-1} \text{ mol}^{-1}$; $\text{H}_2(\text{g})$: $28.84 \text{ J K}^{-1} \text{ mol}^{-1}$; $\text{O}_2(\text{g})$: $29.37 \text{ J K}^{-1} \text{ mol}^{-1}$.

