

3. Basic Concepts of Thermodynamics – Part 2

Temperature and Heat

If you take a can of cola from the refrigerator and leave it on the kitchen table, its temperature will rise-rapidly at first but then more slowly-until the temperature of the cola equals that of the room (the two are then in **thermal equilibrium**). In the same way, the temperature of a cup of hot coffee, left sitting on the table, will fall until it also reaches room temperature.

In generalizing this situation, we describe the cola or the coffee as a **system** (with temperature T_S) and the relevant parts of the kitchen as the **environment** (with temperature T_E) of that system. Our observation is that if T_S is not equal to T_E , then T_S will change (T_E may also change some) until the two temperatures are equal and thus thermal equilibrium is reached.

Such a change in temperature is due to the transfer of a form of energy between the system and its environment. This energy is **internal energy** (or **thermal energy**).

The **transferred internal energy** is called **heat** and is symbolized Q .

- Heat is **positive** when internal energy is transferred to a

system from its environment (we say that heat is absorbed). Thus, when $T_S < T_E$, $Q > 0$.

- Heat is *negative* when internal energy is transferred from a system to its environment (we say that heat is released or lost). Thus, when $T_S > T_E$, $Q < 0$.
- When $T_S = T_E$, $Q = 0$; there will be no heat transfer between the system and the environment; *they are in thermal equilibrium*.

Heat is the energy that is transferred between a system and its environment because of a temperature difference that exists between them.

Recall that energy can also be transferred between a system and its environment by means of *work* W , which we always associate with a force acting on a system during a displacement of the system. Heat and work, unlike temperature, pressure, and volume, are not intrinsic properties of a system. They have meaning only as they describe the transfer of energy into or out of a system.

Units for heat

Before scientists realized that heat is transferred energy, heat was measured in terms of its ability to raise the temperature of water.

- Thus the *calorie (cal)* was defined as the amount of heat that would raise the temperature of 1 g of water from 14.5°C to 15.5°C.
- In the British system, the corresponding unit of heat was the British *thermal unit (Btu)*, defined as the amount of heat that would raise the temperature of 1 lb of water from 63°F to 64°F.

- In 1948, the scientific community decided that since heat (like work) is transferred energy, the SI unit for heat should be the same as that for energy, namely, the joule.

The calorie is now defined to be 4.1860 J (exactly) with no reference to the heating of water. (The "calorie" used in nutrition, sometimes called the Calorie (Cal), is really a kilocalorie.) The relations among the various heat units are

$$1 \text{ cal} = 3.969 \times 10^{-3} \text{ Btu} = 4.186 \text{ J}.$$

The Absorption of Heat by Solids and Liquids

Heat Capacity

The heat capacity C of an object (for example, a Pyrex coffee pot or a marble slab) is the proportionality constant between an amount of heat and the change in temperature that this heat produces in the object. Thus

$$Q = C(T_f - T_i). \quad 1$$

in which T_i and T_f are the initial and final temperatures of the object.

- Heat capacity C has the unit of energy per degree (J/C°) or energy per kelvin (J/K).

Specific Heat

Two objects made of the same material, say marble, will have heat capacities proportional to their masses. It is therefore convenient to define a "heat capacity per unit mass" or specific heat c that refers not to an object but to a unit mass of the material of which the object is made. Eq. 1 then becomes

$$Q = cm (T_f - T_i). \quad 2$$

- Specific heat has the unit J/kg.K.

SPECIFIC HEATS OF SOME
SUBSTANCES
AT ROOM
TEMPERATURE

SUBSTANCE	SPECIFIC HEAT		MOLAR SPECIFIC HEAT
	Cal/g.K	J/kg. K	J/mol. K
<i>Elemental Solids</i>			
Lead	0.0305	128	26.5
Tungsten	0.0321	134	24.8
Silver	0.0564	236	25.5
Copper	0.0923	386	24.5
Aluminum	0.215	900	24.4
<i>Other Solids</i>			
Brass	0.092	380	
Granite	0.19	790	
Glass	0.20	840	
Ice (-10°C)	0.530	2220	
<i>Liquids</i>			
Mercury	0.033	140	
Ethyl alcohol	0.58	2430	
Seawater	0.93	3900	
Water	1.00	4190	

Example: of specific heats (in J/kg.K):

Lead: 128

Water: 4190

Seawater: 3900

What material will require more heat to raise its temperature by 1K?

Molar Specific Heat

In many instances the most convenient unit for specifying the amount of a substance is the **mole (mol)**, where

$$1 \text{ mol} = 6.02 \times 10^{23} \text{ elementary units of any substance}$$

Example: 1 mol of aluminum means 6.02×10^{23} atoms (the atom being the elementary unit), and 1 mol of aluminum oxide means 6.02×10^{23} molecules of the oxide (because the molecule is the elementary unit of a compound).

When quantities are expressed in moles, the specific heat must also involve moles (rather than a mass unit); it is then called a **molar specific heat (the unit in this case is J / mol.K)**.

The table shows the values for some elemental solids (each consisting of a single element) at room temperature.

SUBSTANCE	SPECIFIC HEAT		MOLAR SPECIFIC HEAT
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Note that the molar specific heats of all the elements listed in the table have about the same value at room temperature, namely, **25 J/mol. K**.

- As a matter of fact, the molar specific heats of all solids increase toward that value as the temperature increases.
- Some substances, such as carbon and beryllium, do not reach this limiting value until temperatures well above room temperature.
- Other substances may melt or vaporize before they reach this limit.

When we compare two substances on a molar basis, we are comparing samples that contain the same number of elementary units. The fact that at high enough temperatures, **all solid elements have the same molar specific heat tells us that atoms of all kinds-whether they are aluminum, copper, uranium, or anything else-absorb heat in the same way.**

Note: In determining and then using the specific heat of any substance, we need to know the conditions under which heat transfer occurs. For solids and liquids, we usually assume that the sample is under constant pressure (usually atmospheric) during the heat transfer. It is also conceivable that the sample is held at constant volume while the heat is absorbed. This means that thermal expansion of the sample is prevented by applying external pressure. For solids and liquids, this is very hard to arrange experimentally but the effect can be calculated, and it turns out that

- **The specific heats under constant pressure and constant volume for any solid or liquid differ usually by no more than a few percent.**
- Gases, as you will see, have quite different values for their specific heats under constant-pressure conditions and under constant-volume conditions.

Heats of Transformation

When heat is absorbed by a solid or liquid, the temperature of the sample does not necessarily rise. Instead, the sample may **change from one phase**, or **state**, (that is, solid, liquid, or gas) to another. Thus ice may melt and water may boil, absorbing heat in each case without a temperature change. In the reverse processes (water freezing, steam condensing), heat is released by the sample, again while the temperature of the sample remains constant.

The amount of heat per unit mass that must be transferred when a sample completely undergoes a phase change is called the heat of transformation L .

So when a sample of mass m completely undergoes a phase change, the total heat transferred is

$$Q = Lm.$$

- When the phase change is from solid to liquid (then the sample must absorb heat) or from liquid to solid (then the sample must release heat), the heat of transformation is called the **heat of fusion** L_F . For water at its normal freezing or melting temperature, $L_F = 333 \text{ kJ/kg}$.
- When the phase change is from liquid to gas (then the sample must absorb heat) or from gas to liquid (then the sample must release heat), the heat of transformation is called the **heat of vaporization** L_V . For water at its normal boiling or condensation temperature $L_V = 2256 \text{ kJ/kg}$.

Example: A candy bar has a marked nutritional value of 350 Cal. How many kilowatt-hours of energy will it deliver to the body as it is digested?

Answer: 0.407 kW.h

Note: This amount of energy would keep a 100 W light bulb burning for 4.1 h. To burn up this much energy by exercise, a person would have to jog about 3 or 4 mi.

A generous human diet corresponds to about 3.5 kW.h per day, which represents the absolute maximum amount of work that a human can do in one day. In an industrialized country, this amount of energy can be purchased (perhaps as electrical energy) for about 35 cents.

Example: How much heat is needed to take ice of mass $m = 720$ g at -10°C to a liquid state at 15°C ?

Answer: 300 kJ.

Example: A copper slug whose mass m_c is 75 g is heated in a laboratory oven to a temperature T of 312°C . The slug is then dropped into a glass beaker containing a mass $m_w = 220$ g of water. The heat capacity C_b of the beaker is 45 cal/K. The initial temperature T_j of the water and the beaker is 12°C . What is the final temperature T_f of the slug, the beaker, and the water when thermal equilibrium is reached?

Answer: 20°C

The Absorption of Heat by gases

The heat capacity can be written as:

$$C = \frac{dQ}{dT} \quad 1$$

The heat absorbed by a gas depends on the path.

Heat capacity at constant volume

If a gas is heated with its volume constant, then the measured heat capacity is called the heat capacity at constant volume and is denoted by the symbol C_V .

At constant volume the heat absorbed increases the energy of the system when the temperature is raised from T_1 to T_2 , i.e.

$$C_V(T_2 - T_1) = U_2 - U_1. \quad 2$$

For a very small change dT in temperature, the heat capacity at constant volume is equal to the rate of change of internal energy with temperature, i.e.

$$C = \frac{dU}{dT} \quad 3$$

Heat capacity at constant pressure

If a gas is heated with the pressure fixed, the measured heat capacity is called the heat capacity at constant pressure, C_P . When heat is supplied to a system at constant pressure, expansion occurs and therefore work is done against the applied (external) pressure. Consequently, more heat is required to produce a 1°C rise in temperature at constant pressure than at constant volume. The extra heat needed goes into the work done in expansion, i.e.

$$C_P = C_V + \text{heat for work done in expansion.} \quad 4$$

Experimental information about the C_P of a substance may often be represented with considerable precision by an empirical equation. With some substances, such as H₂O, the value of C_P is nearly a linear function of temperature and, therefore, may be represented by the equation

$$C_P = a + bT \quad 5$$

In order to represent the data for other substances it may be necessary to add a third term to Equation 5

$$C_P = a + bT + cT^\alpha \quad 6$$

Where α can have values of 2 or -1 or -2, etc.

It is possible to compute the heat required to increase the temperature of a substance over any interval within the range of experimental temperatures. Thus, Eq. 1 becomes:

$$Q = \int_{T_1}^{T_2} C dT \quad 7$$

If the experimental values of C are available over the temperature interval of interest, the value of Q in Eq. 7 may be obtained graphically. When the heat capacity is known as a function of temperature in the form of an empirical equation such as Eq. 6, the integral in Eq. 7 becomes

$$Q = \int_{T_1}^{T_2} (a + bT + cT^\alpha) dT \quad 8$$

The molar heat capacity of a substance depends on its temperature.

Example: it takes 75.22 J/mol °C to raise the temperature of 1 mol of water from 25 to 26°C, and 75.8 J/mol °C to raise it from 95 to 96°C. It is, therefore, more precise to define the molar heat capacity C_x by the differential relationship

$$dQ_x = nC_x dT \quad 9$$

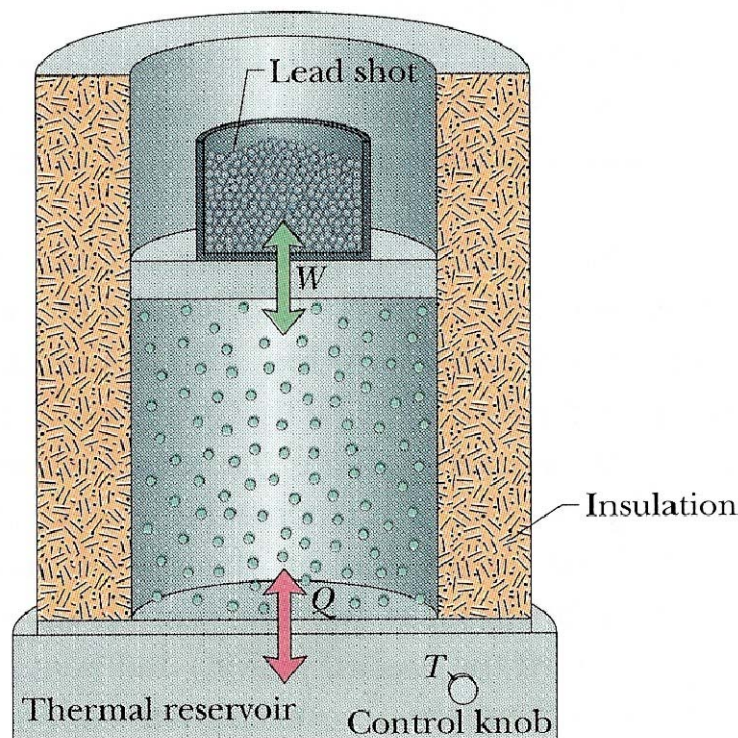
where dQ_x is the heat required to raise the temperature of n mols of substance from T to $T + dT$ along the path x .

The change in C_P and C_V with temperature, in a range of some ten or even hundred degrees Celsius, is usually small and neglected unless indicated otherwise. Thus, if n mols of a substance are to be heated (or cooled) isobarically from T_1 to T_2 , the amount of heat involved is

$$Q \cong n C_P (T_2 - T_1) = n C_P \Delta T \quad 10$$

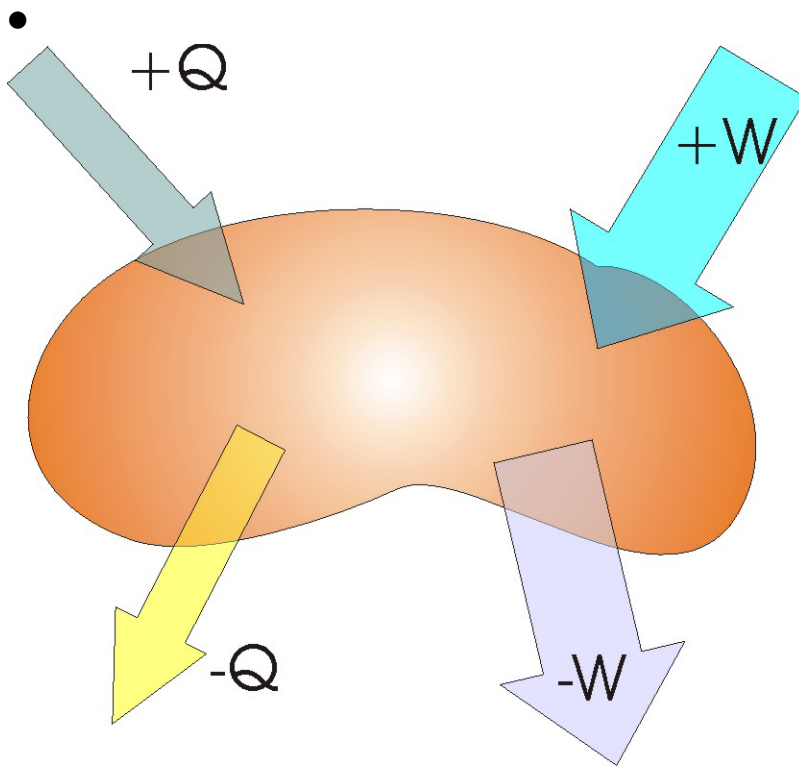
Heat and work

Here we look in some detail at how heat and work are exchanged between a system and its environment. Let us take as our system a gas confined to a cylinder with a movable piston, as in figure below.



- The upward force on the piston due to the pressure of the confined gas is equal to the weight of lead shot loaded onto the top of the piston.
- The walls of the cylinder are made of insulating material that does not allow any heat transfer.
- The bottom of the cylinder rests on a reservoir for thermal energy, a *thermal reservoir* (perhaps a hot plate) whose temperature T you can control by turning a knob.
- The system (the gas) starts from an *initial state* i , described by a pressure P_i a volume V_i , and a temperature T_i .

- You want to change the system to a *final state* f described by a pressure P_f a volume V_f and a temperature T_f .
- During the change from state i to state f , heat may be transferred into the system from the thermal reservoir (**positive heat**) or vice versa (**negative heat**). And work is done by the system to raise the loaded piston (**negative work**) or lower it (**positive work**).



- We assume that all such changes occur slowly, with the result that the system is always in (approximate) thermal equilibrium, (that is, every part of the system is always in thermal equilibrium with every other part).
- Suppose that you remove a few lead shot from the piston, allowing the gas to push the piston and remaining shot upward through a differential displacement ds with an upward force F . Since the displacement is tiny, we can assume that F is constant during the displacement. Then F has a magnitude that is equal to PA , where P is the pressure of the gas and A is the face area of

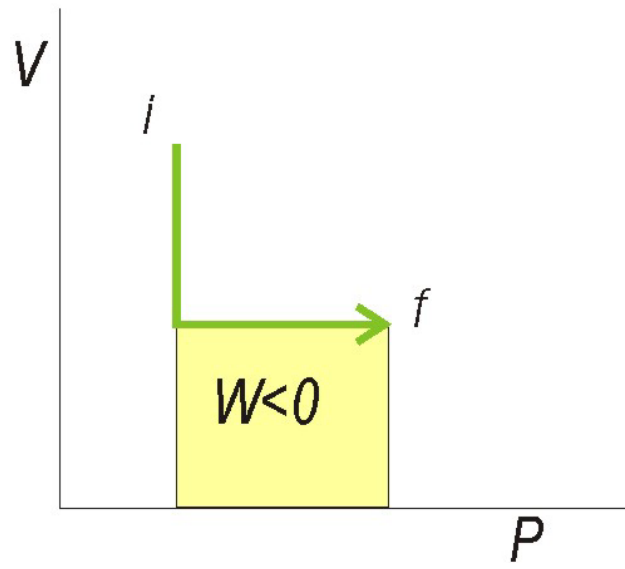
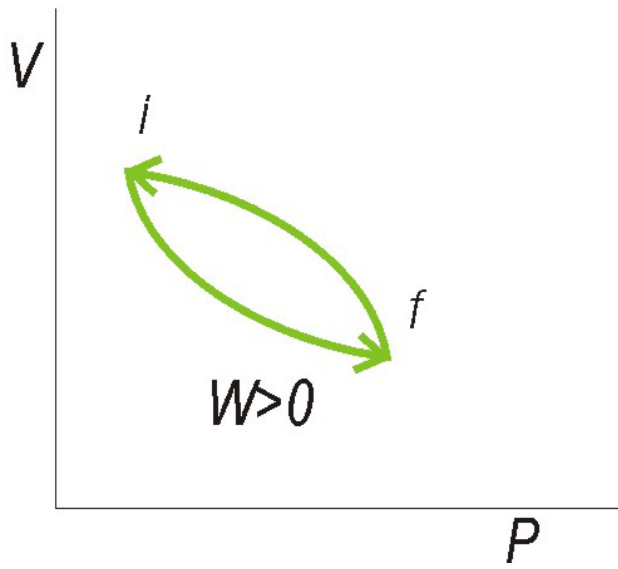
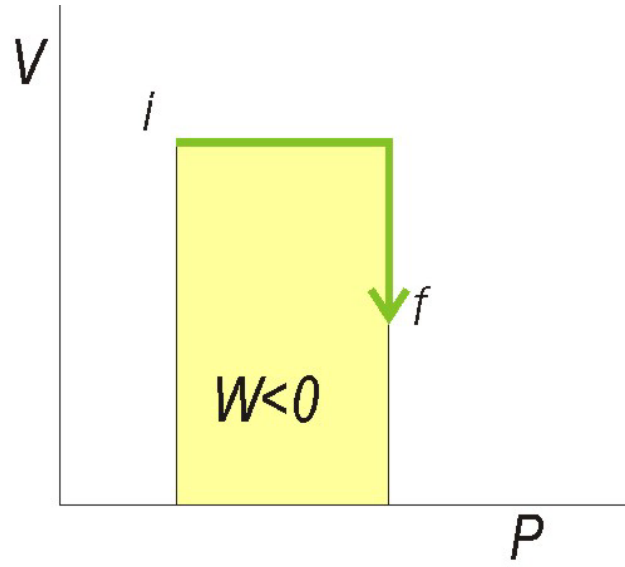
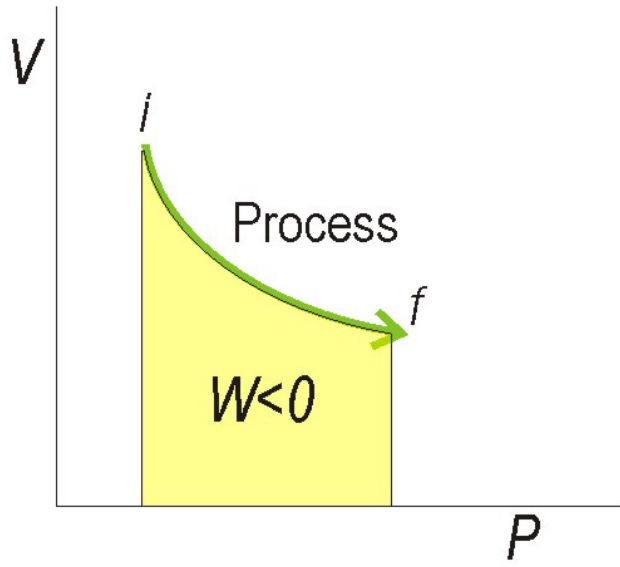
the piston. The differential work dW done by the gas during the displacement is

$$dW = F ds = (PA)(ds) = PdV \quad 11$$

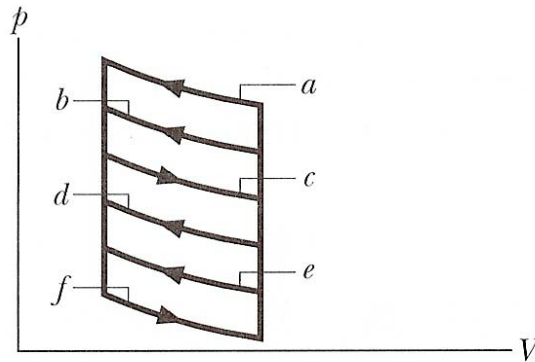
When the overall volume changes from V_i to V_f , the total work done by the gas is:

$$W = \int dW = \int_{V_1}^{V_2} PdV \quad 12$$

- During the change in volume, the pressure and temperature of the gas may also change. To evaluate the integral in Eq. 12 directly, we would need to know how pressure varies with volume for the actual process by which the system changes from state i to state f .



Example: The P - V diagram shows six curved paths (connected by vertical paths) that can be followed by a gas. Which two of them should be part of a closed cycle if the net work done on the gas is to be at its maximum positive value?



In the important special case in which the outside pressure remains constant during a finite expansion of the system, P may be brought outside the integral sign, so that

$$W = P \int_1^2 dV = P\Delta V$$

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This equation shows that, when $P = 0$, i.e. when the external pressure is zero, the work $W = 0$. *A system that expands into a vacuum therefore performs no work.*

Let us consider the reversible expansion of an ideal gas at constant temperature T , in which the external pressure P_{ext} is successively reduced so that it always balances the internal pressure P_{int} .

Note: The ideal gases equation as we will see later is:

$$PV = nRT$$

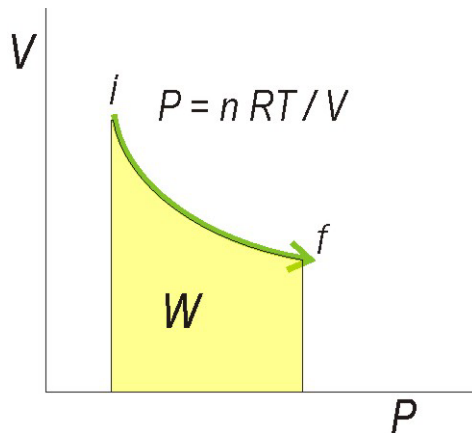
where R is the Universal gas constant.

By the ideal gas equation:

$$P_{ext} = P_{int} = \frac{nRT}{V}$$

thus,

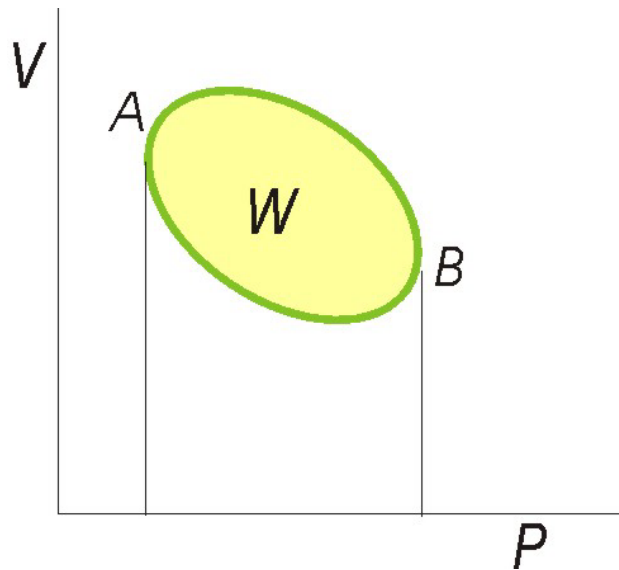
$$W = -\int_1^2 P_{ext} dV = -nRT \int_1^2 \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} \quad 14$$



The yellow area represents the **work performed by the system** and is, therefore, equal to $-W$. As will be seen later, heat has to be supplied to the system to keep the temperature of the expanding gas constant.

- When a system contracts, W is positive because the surroundings now perform work on the system.

- For a cyclic process involving pressure-volume work only, W is the area enclosed by the path in a P - V diagram. W is a positive area when the path corresponds to counter-clockwise rotation, and a negative area for clockwise rotation.



Note: When a gas is changed from V_1 and P_1 to V_2 and P_2 at constant T it can be done many ways, and the W values obtained may be different for any two of these ways.

- The gas may be expanded along a **reversible path**. This is indeed the path for which the integral of $P_{ext} dV$ for the change in state considered is a maximum. All along this path, $P_{ext} = P_{int}$ (except for an infinitesimal amount), and at no point could P_{ext} be increased (thus increasing the integral) without changing the expansion into a compression. The outside pressure may, however, be made smaller than P_{int} for any portion of the path. For this changed portion of the path the contribution to the integral would be decreased, and in addition the expansion would not be reversible because it could not be changed into a compression by an infinitesimal increase of P_{ext} . It is apparent that the reversible path is the only path for which the integral has its maximum value. For any actual path, this integral, the work - W performed by the system on the surroundings, is less than this maximum value. Therefore,

$$- W_{actual} \leq - W_{reversible}$$

Coming attractions:
Enthalpy
Entropy
Law of ideal gases