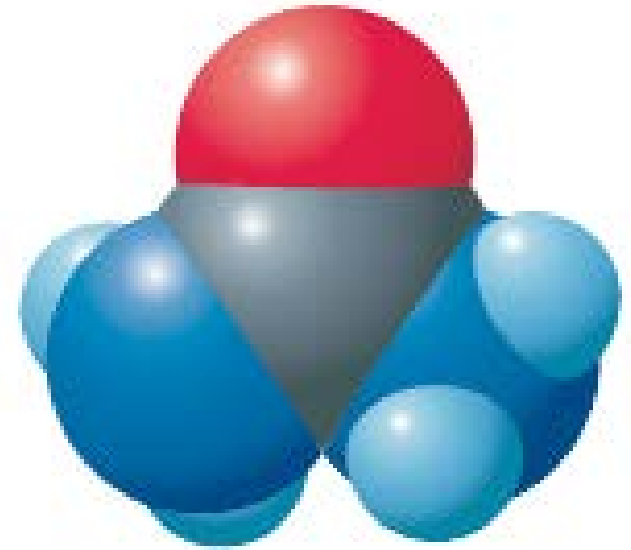


GENERAL CHEMISTRY

THERMODYNAMICS AND EQUILIBRIUM

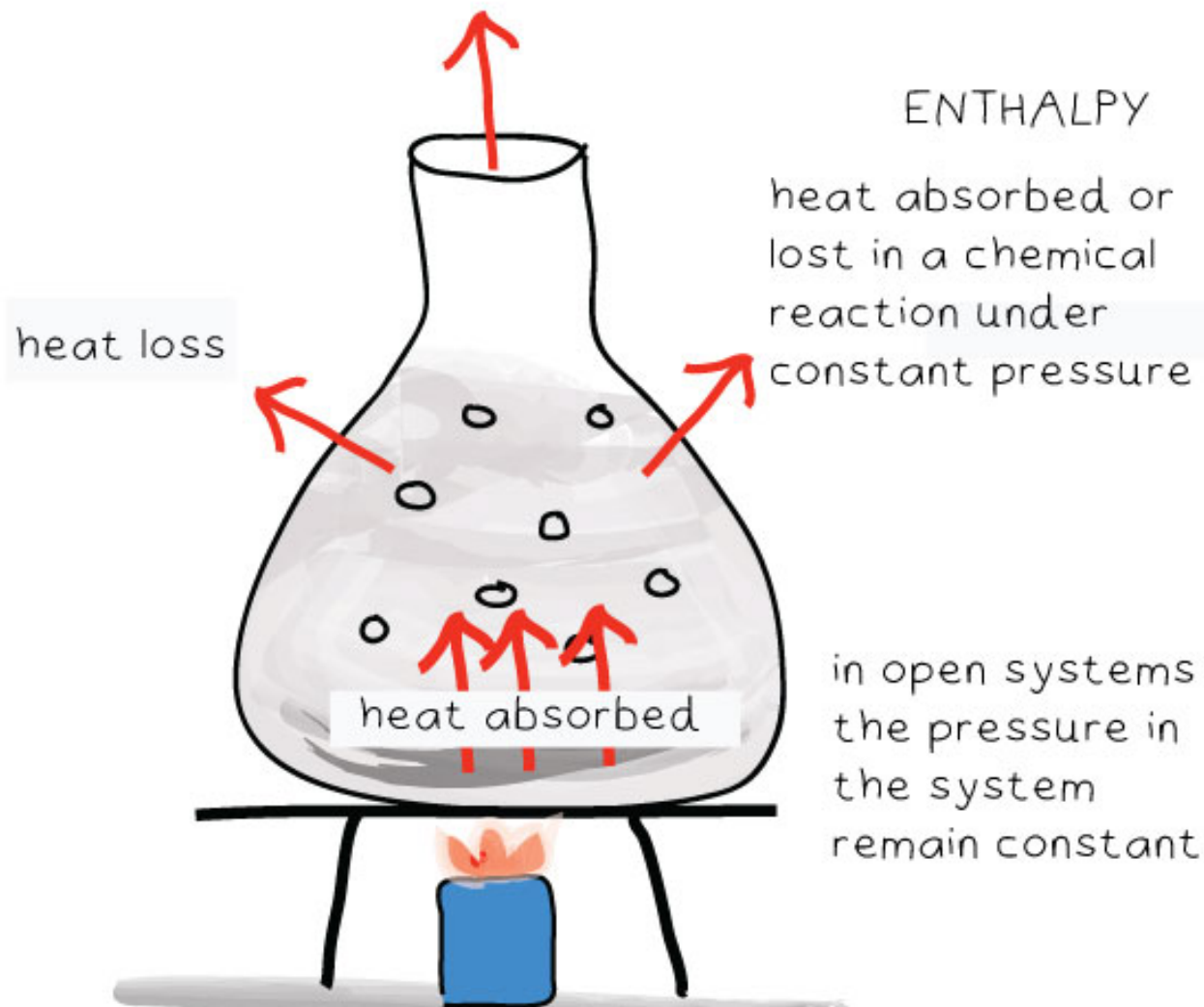
Urea



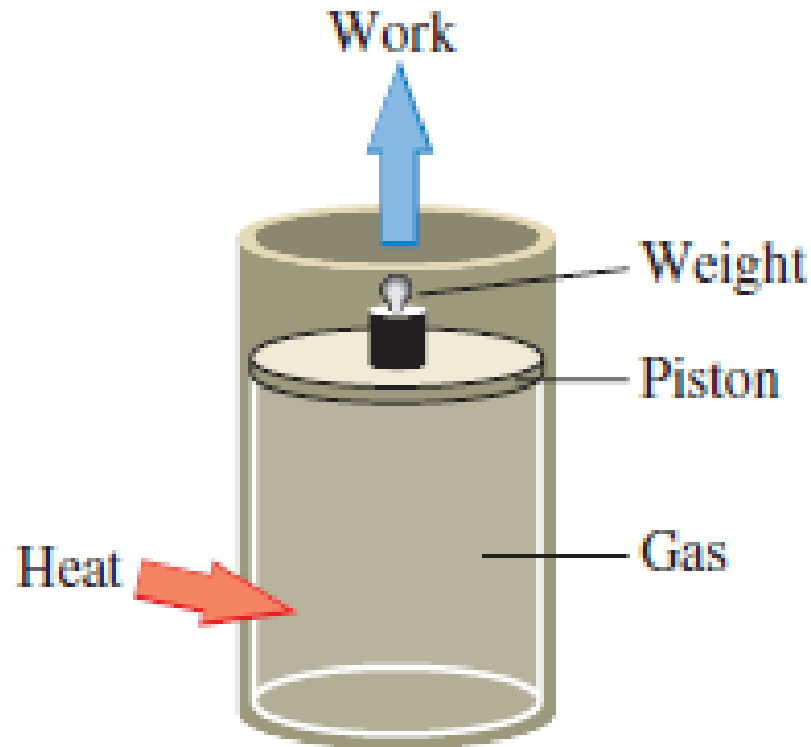
Top: Urea is used as a plant fertilizer because it slowly decomposes in the soil to provide ammonia. *Bottom: A molecular model of urea.*



First Law of Thermodynamics; Enthalpy



Exchanges of heat and work with the surroundings

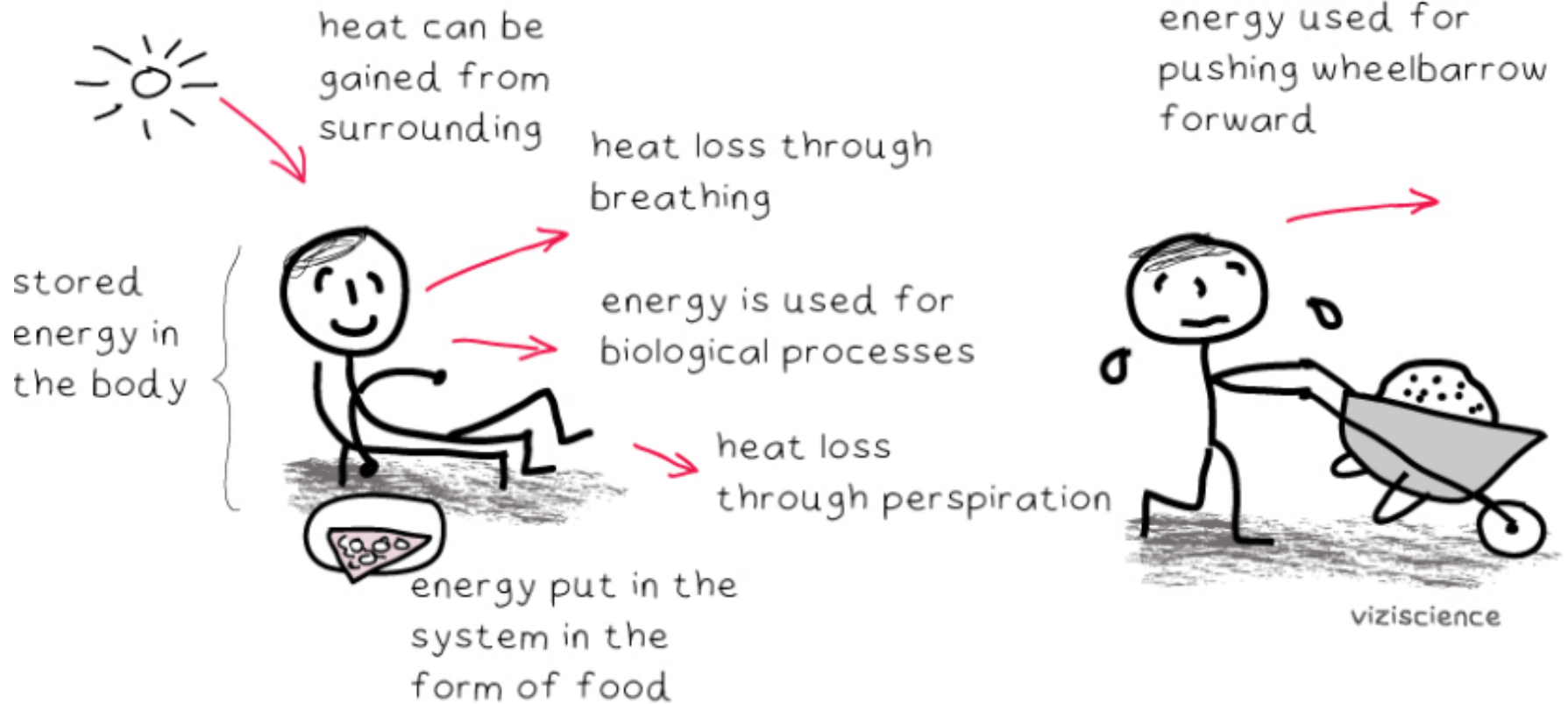


$$\Delta U = q + w$$

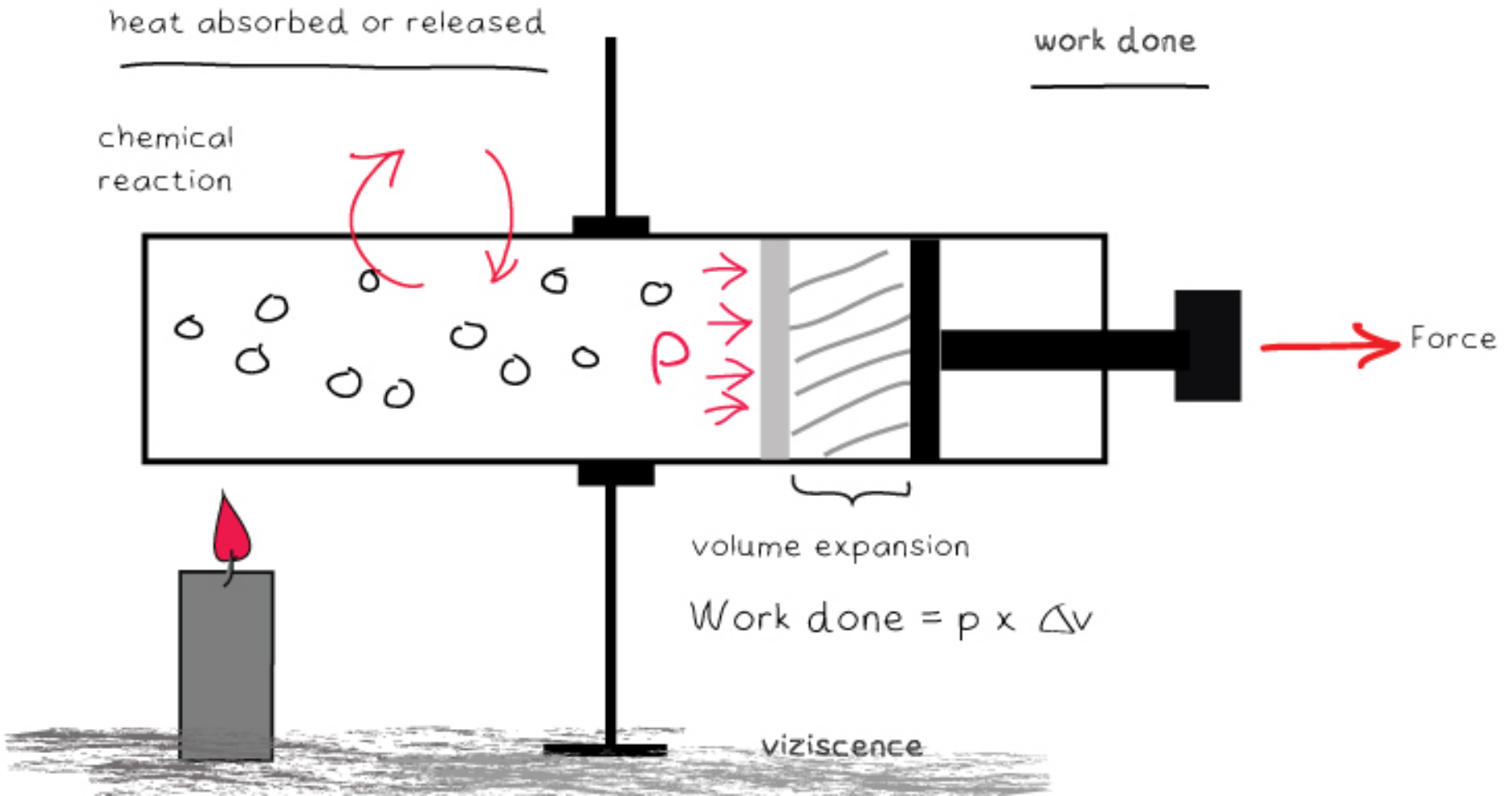
CHANGE IN INTERNAL ENERGY

heat absorbed or released

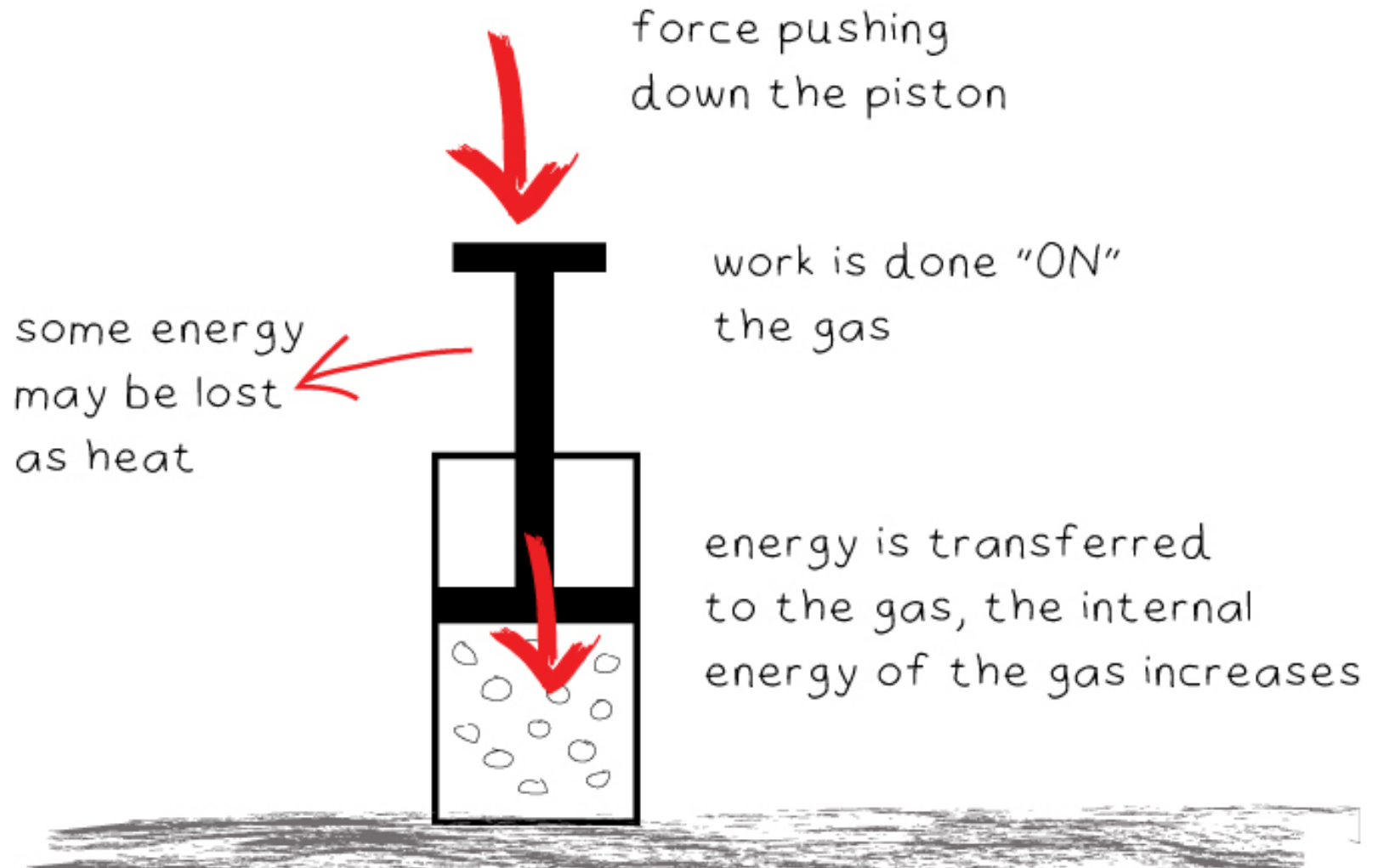
work done



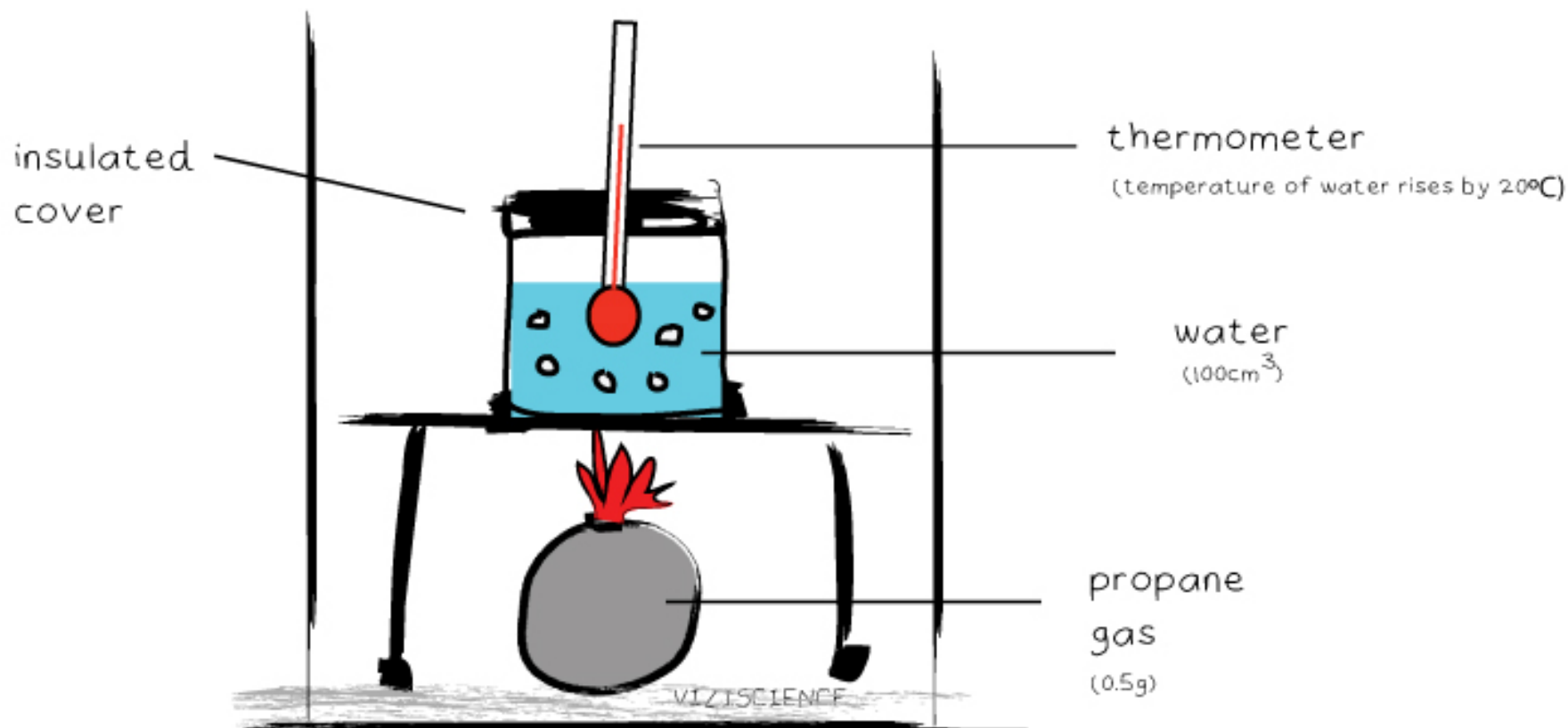
CHANGE IN INTERNAL ENERGY OF A CHEMICAL SYSTEM



WHAT HAPPENS WHEN WORK IS DONE ON THE SYSTEM?

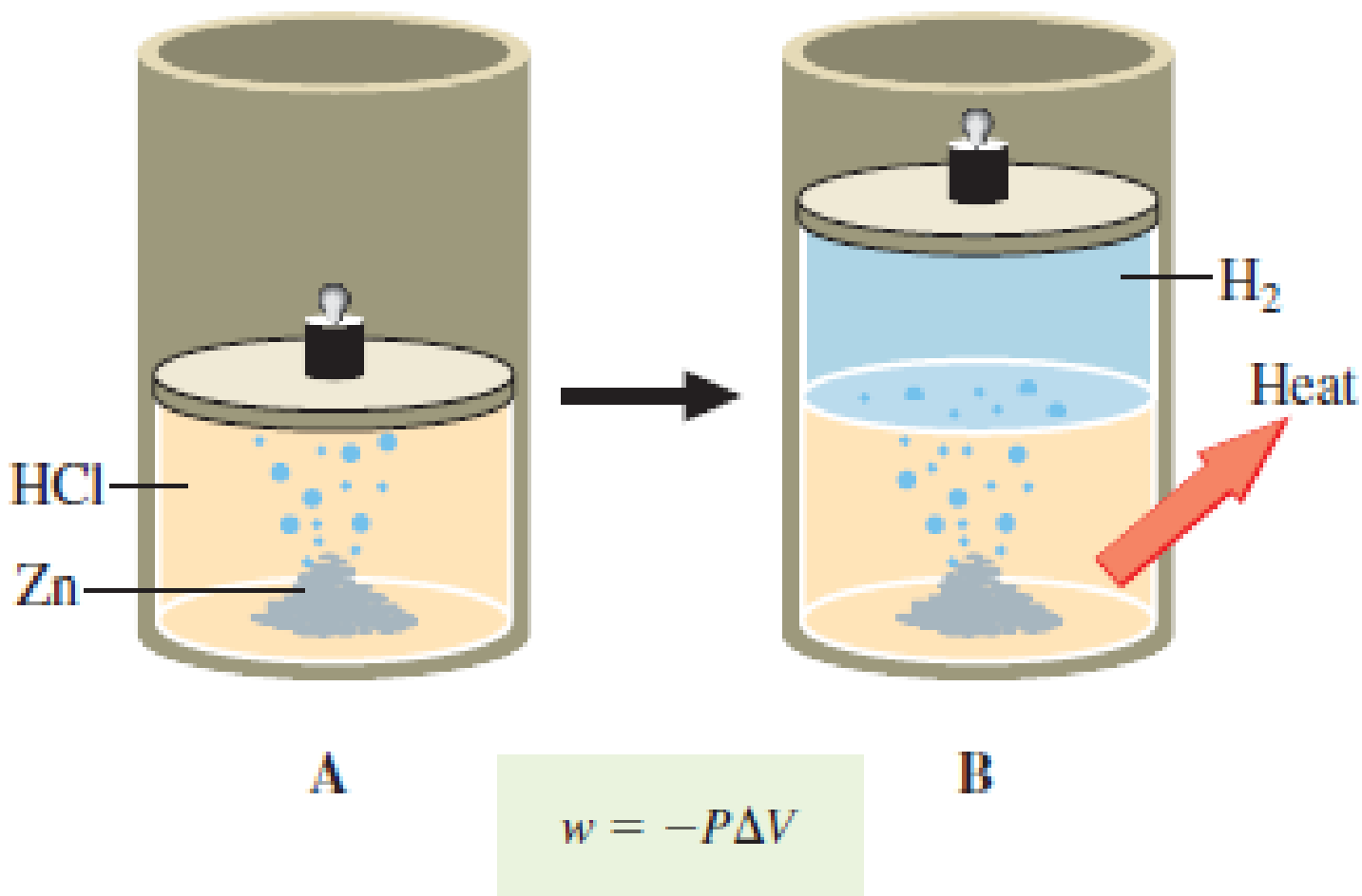


PROPANE COMBUSTION



When 0.5g of propane is burned, the heat produced is used to raise the temperature of 100cm³ of water from 20°C to 40°C. Calculate the enthalpy change (ΔH) for the reaction.

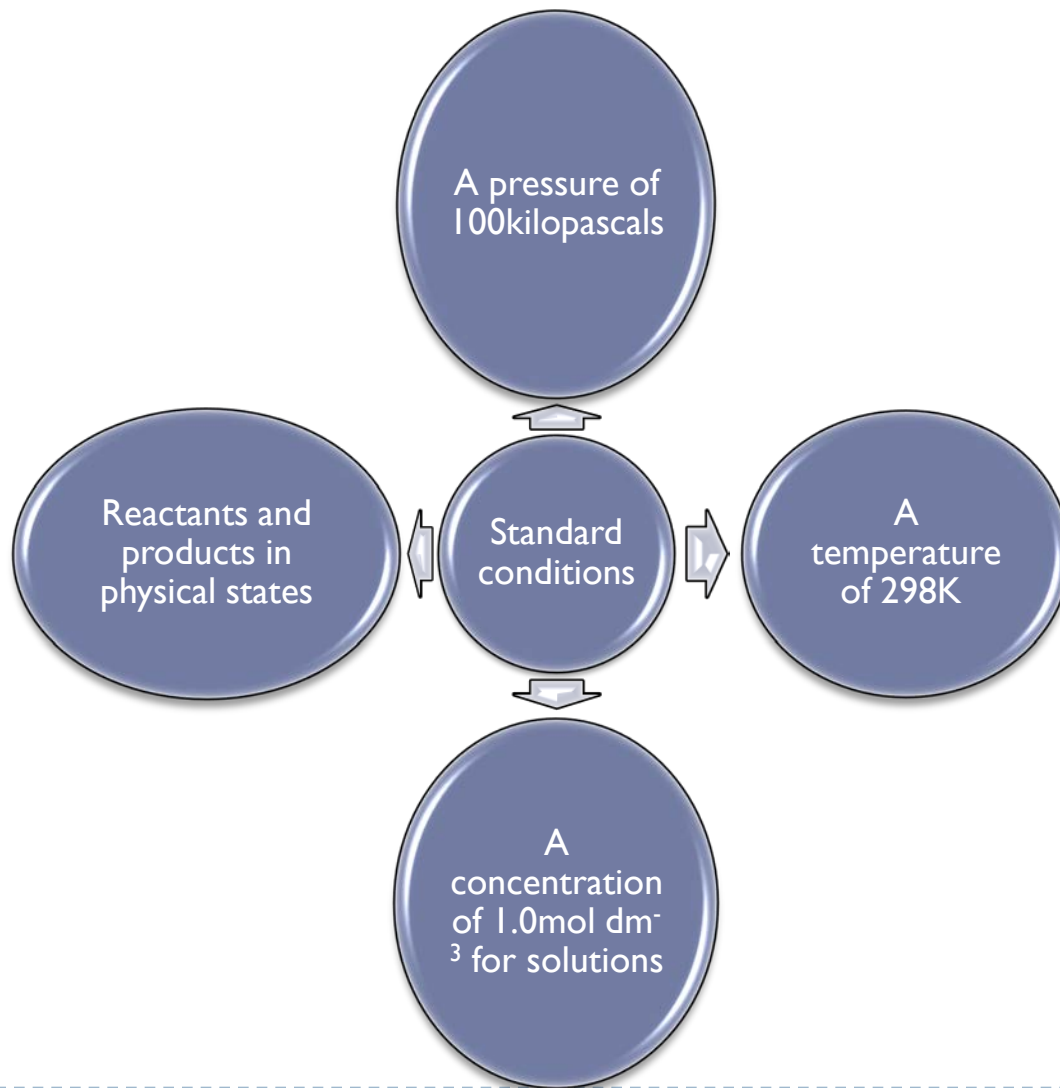
Heat of Reaction and Internal Energy



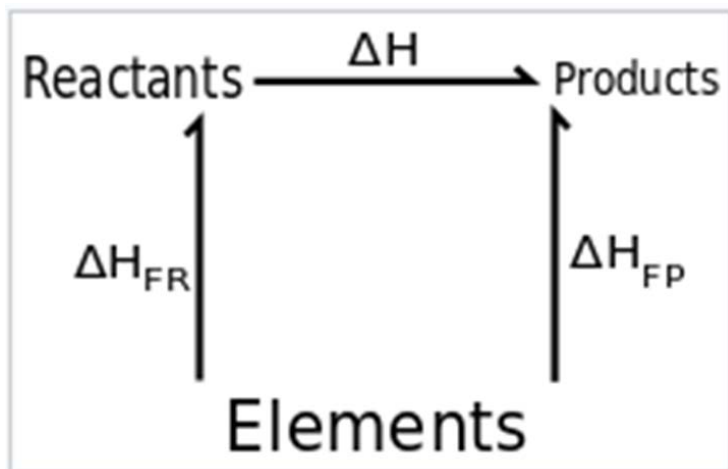
Enthalpy and Enthalpy Change



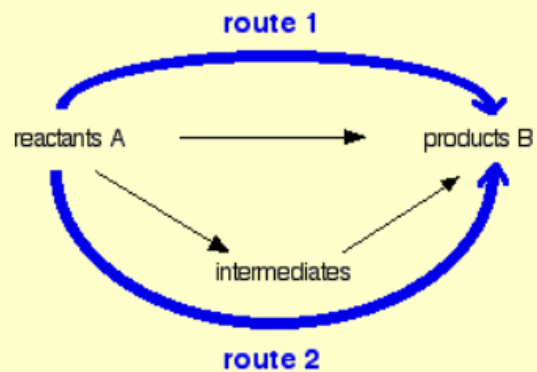
Standard enthalpy changes: standard conditions



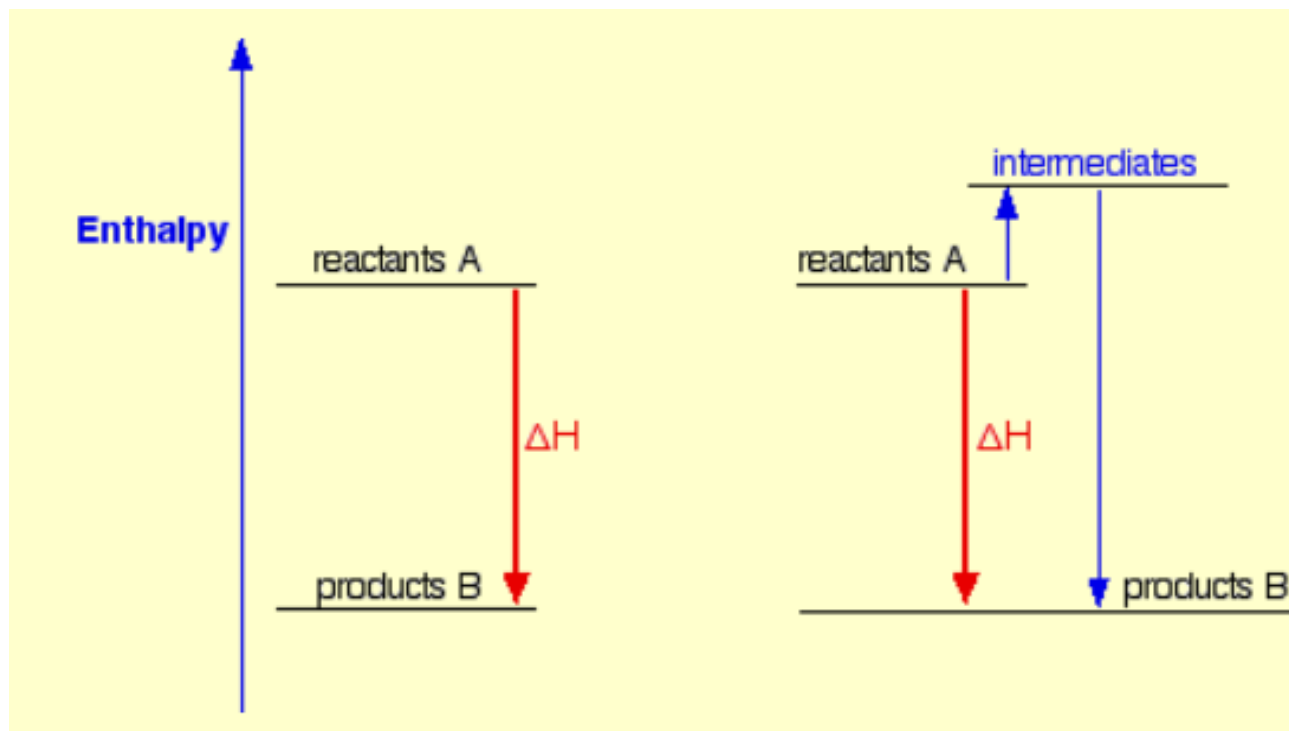
Hess's law



You could set out the above diagram as:



Explaining Hess's Law

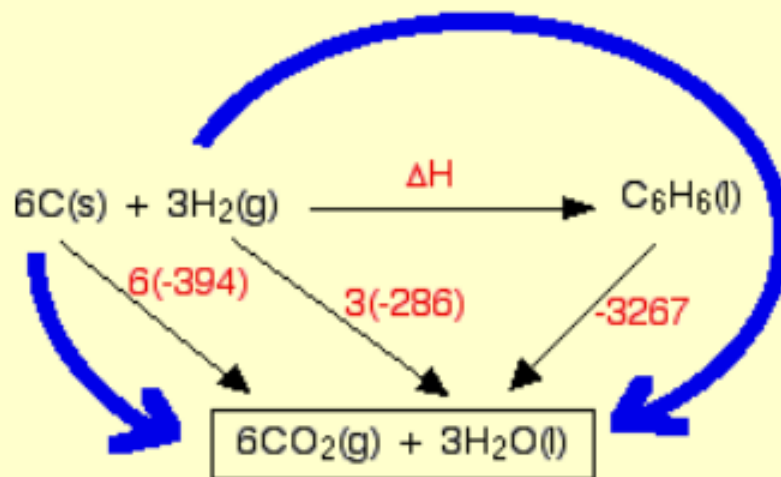


Working out an enthalpy change of formation from enthalpy changes of combustion

Standard enthalpy changes of combustion, ΔH°_c are relatively easy to measure. For benzene, carbon and hydrogen, these are:

	ΔH°_c (kJ mol ⁻¹)
C₆H₆(l)	-3267
C(s)	-394
H₂(g)	-286

In this case, what we are trying to find is the standard enthalpy change of formation of benzene, so that equation goes horizontally



How were the two routes chosen? Remember that you have to go with the flow of the arrows. Choose your starting point as the corner that only has arrows leaving from it. Choose your end point as the corner which only has arrows arriving.

Now do the calculation:

Hess's Law says that the enthalpy changes on the two routes are the same. That means that:

$$\Delta H - 3267 = 6(-394) + 3(-286)$$

Rearranging and solving:

$$\Delta H = 3267 + 6(-394) + 3(-286)$$

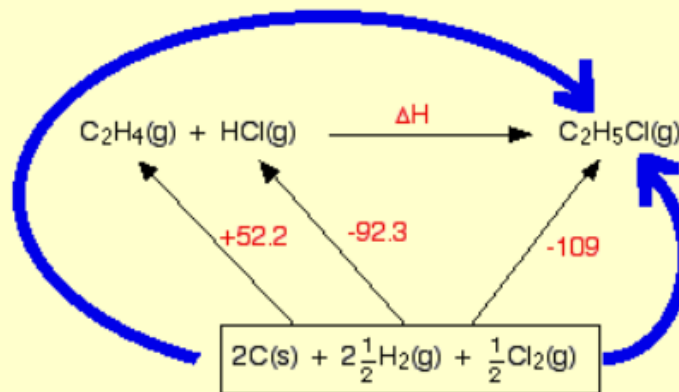
$$\Delta H = +45 \text{ kJ mol}^{-1}$$

Working out an enthalpy change of reaction from enthalpy changes of formation

In this case, we are going to calculate the enthalpy change for the reaction between ethene and hydrogen chloride gases to make chloroethane gas from the standard enthalpy of formation values in the table. If you have never come across this reaction before, it makes no difference

	ΔH°_f (kJ mol ⁻¹)
C₂H₄(g)	+52.2
HCl(g)	-92.3
C₂H₅Cl(g)	-109

In the cycle below, this reaction has been written horizontally, and the enthalpy of formation values added to complete the cycle.



And now the calculation. Just write down all the enthalpy changes which make up the two routes, and equate them

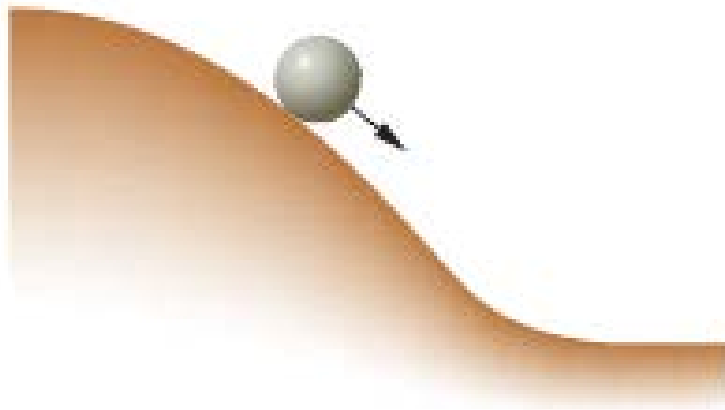
$$+52.2 - 92.3 + \Delta H = -109$$

Rearranging and solving:

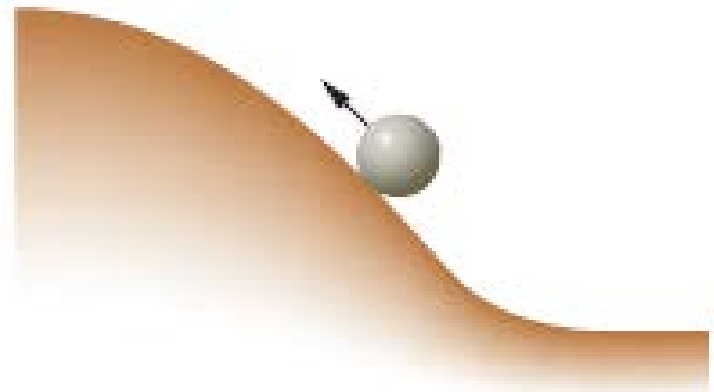
$$\Delta H = -52.2 + 92.3 - 109$$

$$\Delta H = -68.9 \text{ kJ mol}^{-1}$$

Examples of a spontaneous and a nonspontaneous process

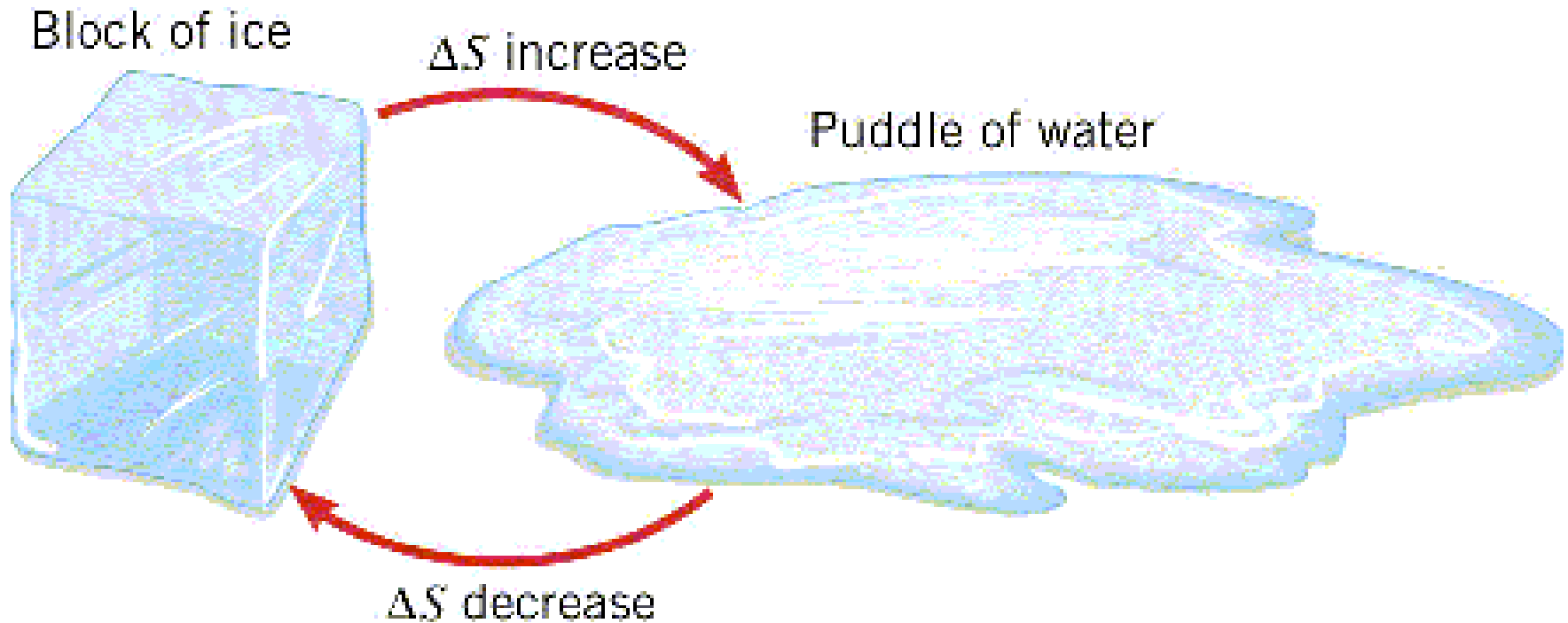


Spontaneous process

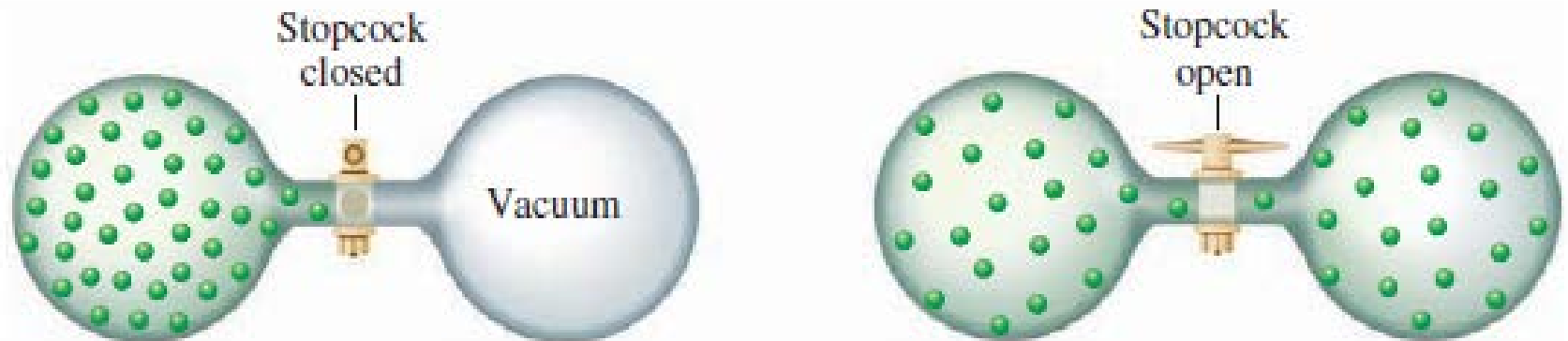


Nonspontaneous process

Entropy and The Second Law of Thermodynamics

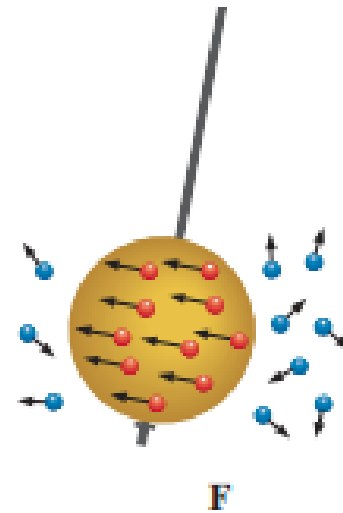
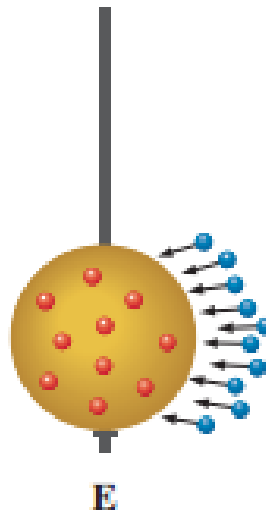
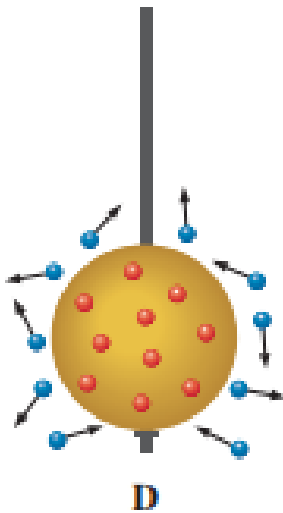
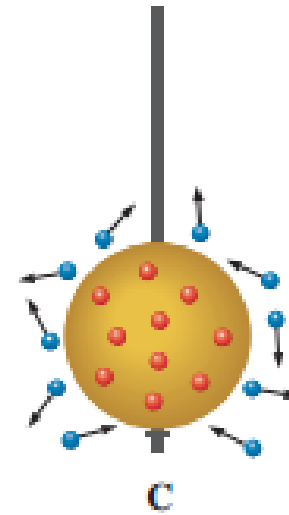
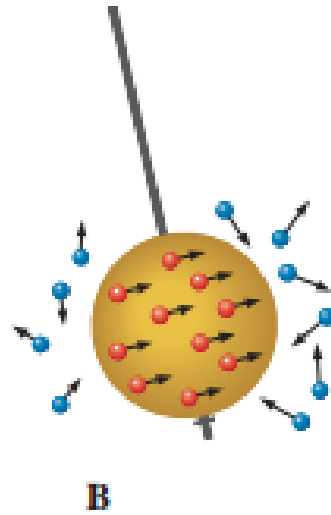
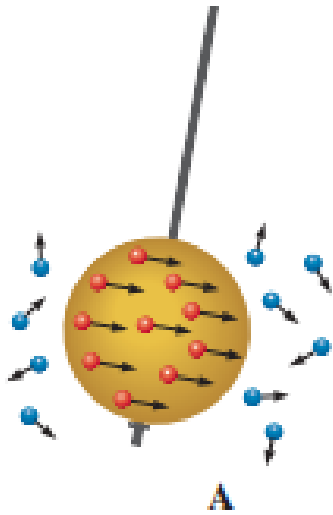


Expansion of a gas into a vacuum



Initially, the flask on the left contains a gas, whereas the flask on the right is evacuated. Then the valve is opened and gas spontaneously flows into the evacuated flask (the vacuum).

Motion of a pendulum

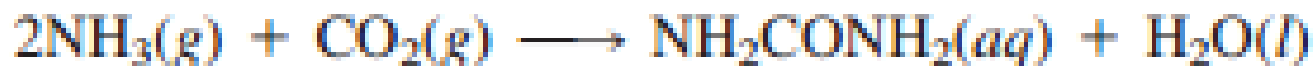


Entropy Change for a Phase Transition

$$\Delta S = \frac{q}{T} \quad (\text{equilibrium process})$$

Criterion for a Spontaneous Reaction

Now we can see how thermodynamics is applied to the question of whether a reaction is spontaneous. Suppose that it is proposed a chemical reaction for the preparation of a substance. Let's assume that the reaction occurs at constant temperature and pressure. For urea, just propose the reaction.



$$\Delta S > \frac{q_p}{T} = \frac{\Delta H}{T} \quad (\text{spontaneous reaction, constant } T \text{ and } P)$$

$$\frac{\Delta H}{T} - \Delta S < 0 \quad (\text{spontaneous reaction, constant } T \text{ and } P)$$

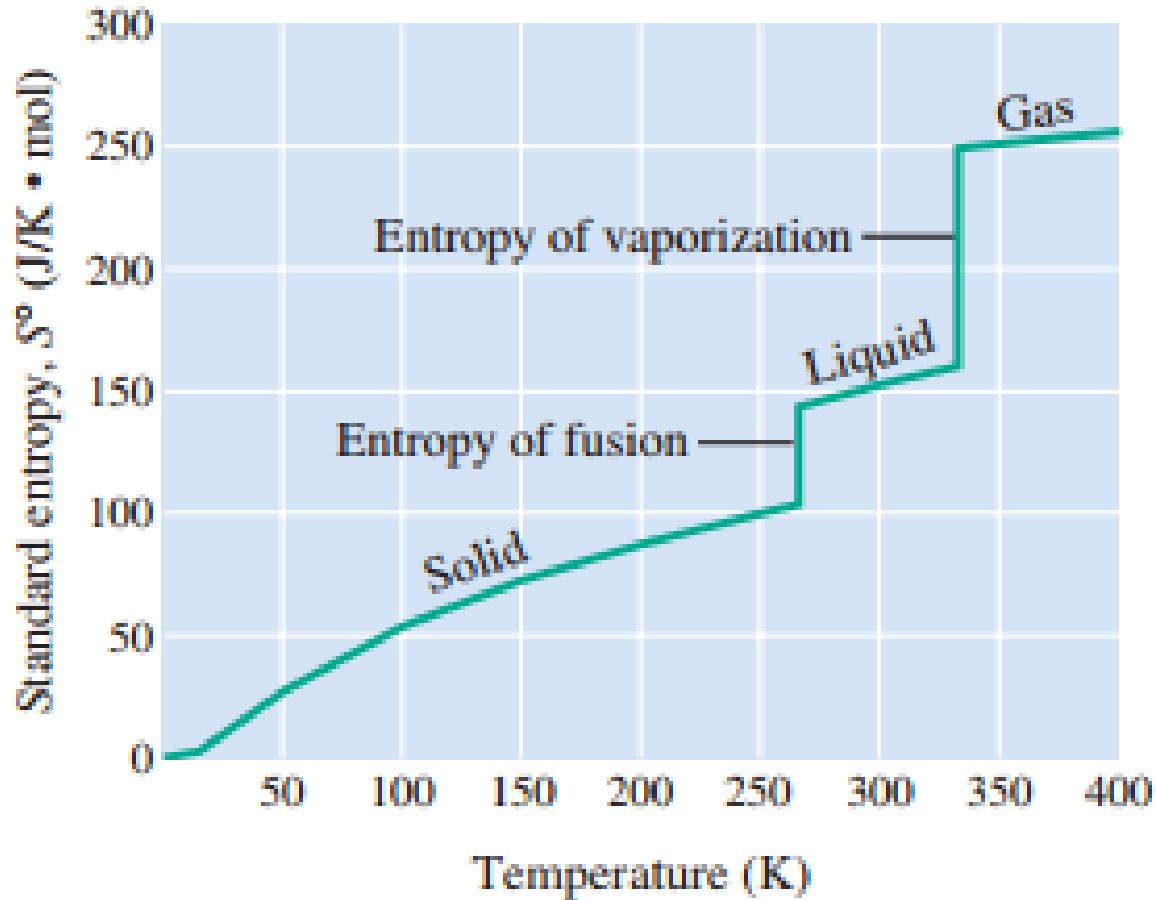
Multiplying each term of this inequality by the positive quantity T , you get

$$\Delta H - T\Delta S < 0 \quad (\text{spontaneous reaction, constant } T \text{ and } P)$$

Third Law of Thermodynamics



Standard entropy of bromine, Br₂, at various temperatures



Entropy Change for a Reaction

The entropy usually increases in the following situations:

1. A reaction in which a molecule is broken into two or more smaller molecules.
2. A reaction in which there is an increase in moles of gas. (This may result from a molecule breaking up, in which case Rules 1 and 2 are related.)
3. A process in which a solid changes to liquid or gas or a liquid changes to a gas.

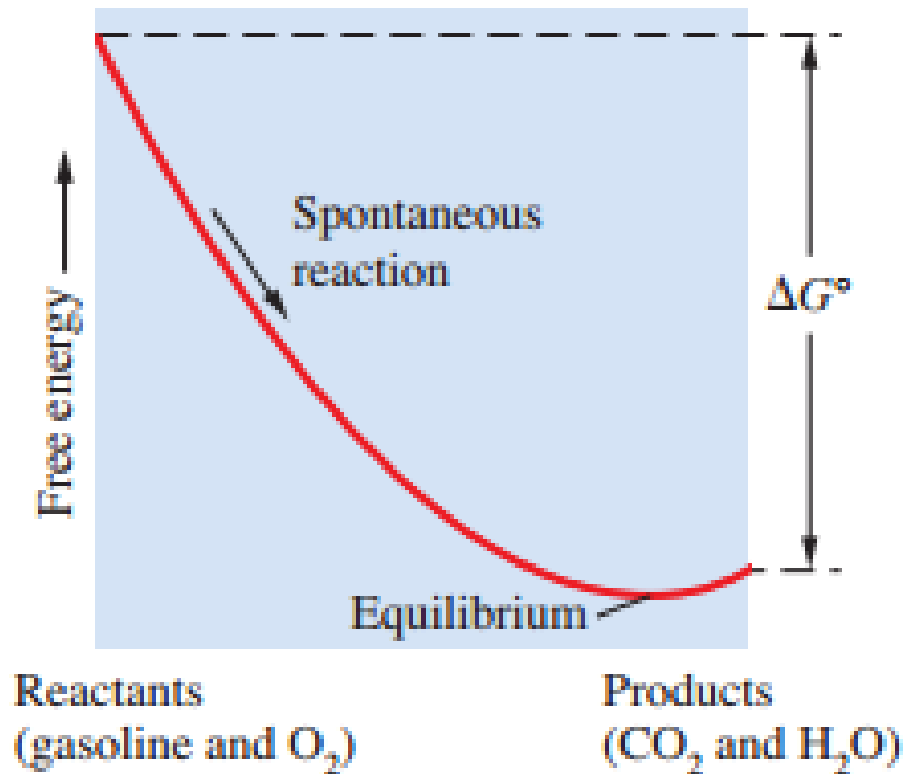
Interpretation of Free Energy

It was seen that the free-energy change serves as a criterion for spontaneity of a chemical reaction. This gives some idea of what free energy is and how to interpret it. In this section, we have a possibility look more closely at the meaning of free energy.

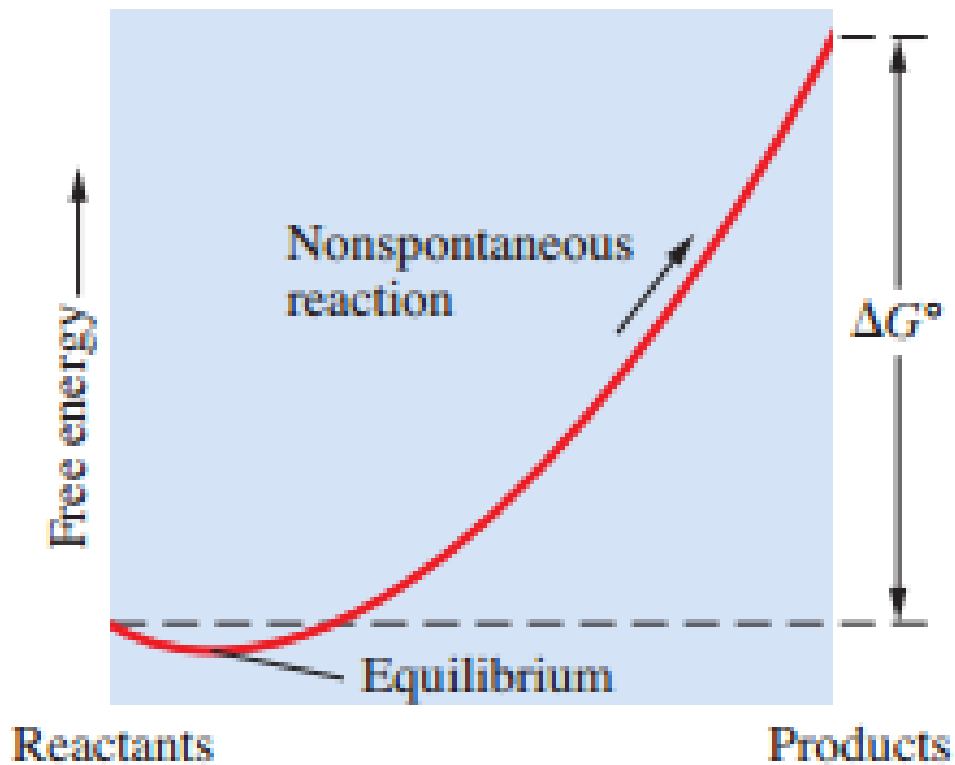


Free-Energy Change During Reaction

Free-energy change during a spontaneous reaction (combustion of gasoline)



Free-energy change during a nonspontaneous reaction



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