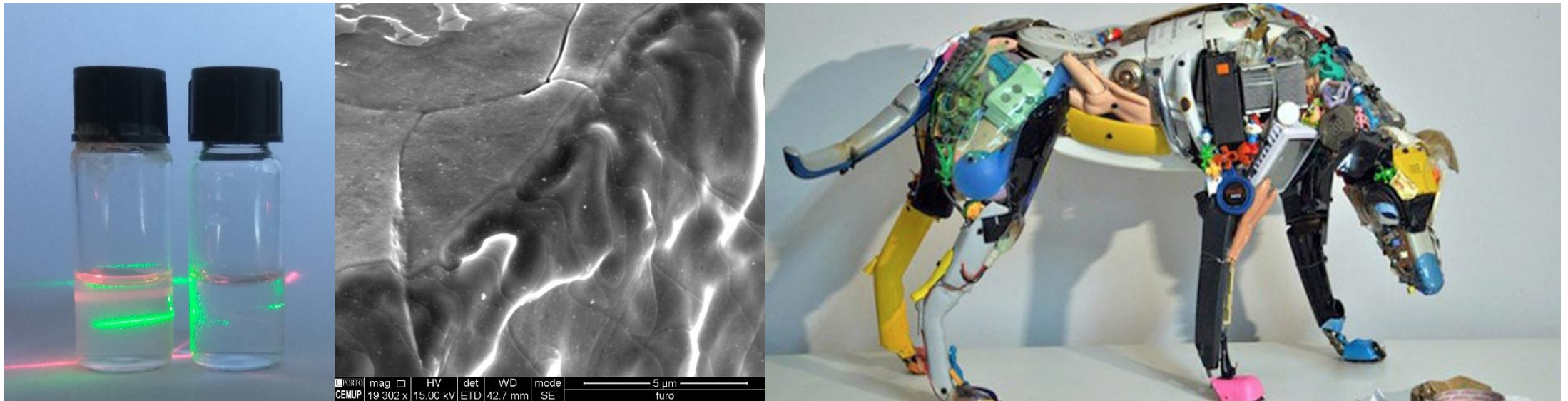# Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.

2.2 The internal energy

In thermodynamics, the total energy of a system is called its **internal energy**
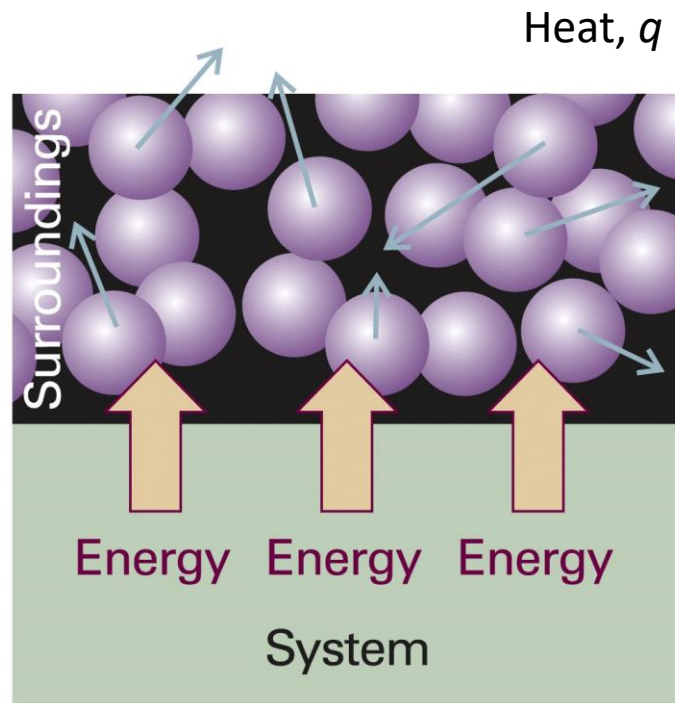

Heat, *q*

Figure 2-3
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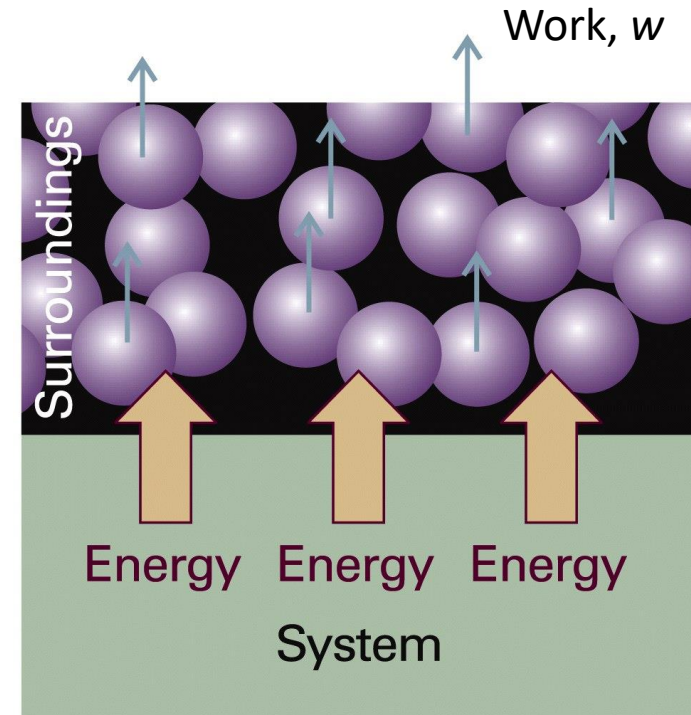© 2006 Peter Atkins and Julio de Paula

Work, *w*

Figure 2-4
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2.2 The internal energy

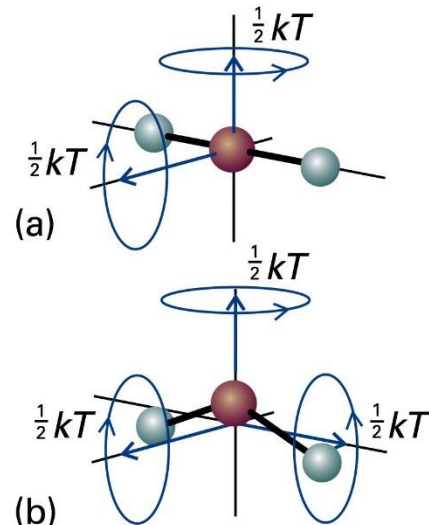In thermodynamics, the total energy of a system is called its **internal energy**,

The internal energy of a gas

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

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

$$U_m = U_m(0) + \tfrac{5}{2}RT \qquad \text{(linear molecule, translation and rotation only)}$$

$$U_m = U_m(0) + 3RT \qquad \text{(nonlinear molecule, translation and rotation only)}$$

$\tfrac{1}{2}kT$

$\tfrac{1}{2}kT$

(a)

$\tfrac{1}{2}kT$

$\tfrac{1}{2}kT$ $\tfrac{1}{2}kT$

(b)

Figure 2-5
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$\tfrac{1}{2}kT$, where k is Boltzmann's constant ($k = 1.381 \times 10^{-23}$ J K^{-1})

2.2 The internal energy

In thermodynamics, the total energy of a system is called its **internal energy**
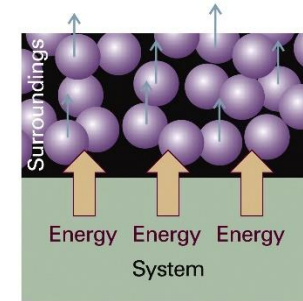
$$\Delta U = q + w$$

$$dU = dq + dw$$

Work, *w*

Heat, *q*

$$\Delta U = q + w$$

$$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V$$

$$w = -\int_{V_i}^{V_f} p_{\mathrm{ex}}\mathrm{d}V$$

External pressure, p_{ex}

$\mathrm{d}z$ $\mathrm{d}V = A\mathrm{d}z$

Area, A Pressure, p

Figure 2-6
Atkins Physical Chemistry, Eighth Edition
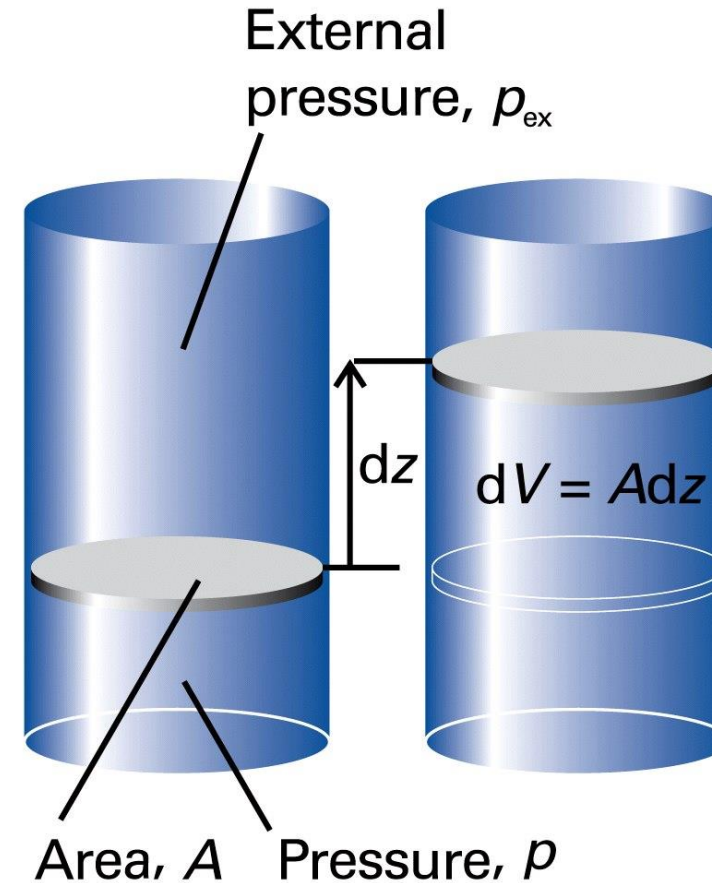© 2006 Peter Atkins and Julio de Paula

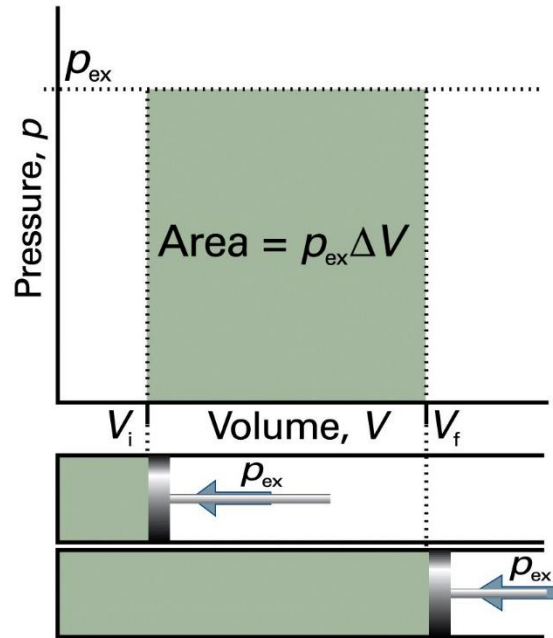## Expansion against constant pressure

Figure 2-7
Atkins Physical Chemistry, Eighth Edition
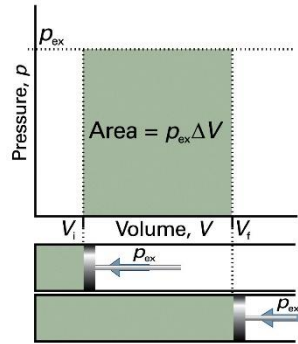© 2006 Peter Atkins and Julio de Paula

$$\mathrm{d}w = -p_{ex}\mathrm{d}V$$

$$w = -\int_{V_i}^{V_f} p_{ex}\mathrm{d}V$$

$$w = -p_{ex}\int_{V_i}^{V_f}\mathrm{d}V = -p_{ex}(V_f - V_i)$$

$$w = -p_{ex}\Delta V$$

Constant pressure

Isothermal reversible
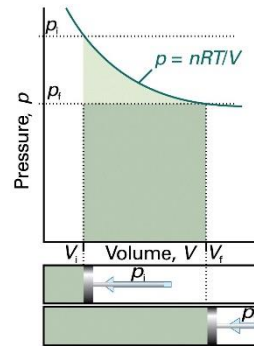
First Law of thermodynamics

The internal energy of an **isolated system** is constant.

$$w = -\int_{V_i}^{V_f} p\,dV$$

Figure 2-7
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Figure 2-8
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$$\Delta U = q + w$$

$$w = -p_{ex}\Delta V$$

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

Figure 2-12
Atkins Physical Chemistry, Eighth Edition
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$$\Delta U = q + w$$

Table 2.1 Varieties of work*

Type of work	$\mathrm{d}w$	Comments	Units†
Expansion	$-p_{ex}\mathrm{d}V$	p_{ex} is the external pressure $\mathrm{d}V$ is the change in volume	Pa m^3
Surface expansion	$\gamma\mathrm{d}\sigma$	γ is the surface tension $\mathrm{d}\sigma$ is the change in area	$N\,m^{-1}$ m^2
Extension	$f\mathrm{d}l$	f is the tension $\mathrm{d}l$ is the change in length	N m
Electrical	$\phi\mathrm{d}Q$	ϕ is the electric potential $\mathrm{d}Q$ is the change in charge	V C

* In general, the work done on a system can be expressed in the form $\mathrm{d}w = -F\mathrm{d}z$, where F is a 'generalized force' and $\mathrm{d}z$ is a 'generalized displacement'.
† For work in joules (J). Note that 1 N m = 1 J and 1 V C = 1 J.

Table 2-1
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$$\Delta U = q + w$$

$U_{\mathrm{m}} = U_{\mathrm{m}}(0) + \frac{3}{2}RT$

$U_{\mathrm{m}} = U_{\mathrm{m}}(0) + \frac{5}{2}RT$ (linear molecule, translation and rotation only)

$U_{\mathrm{m}} = U_{\mathrm{m}}(0) + 3RT$ (nonlinear molecule, translation and rotation only)
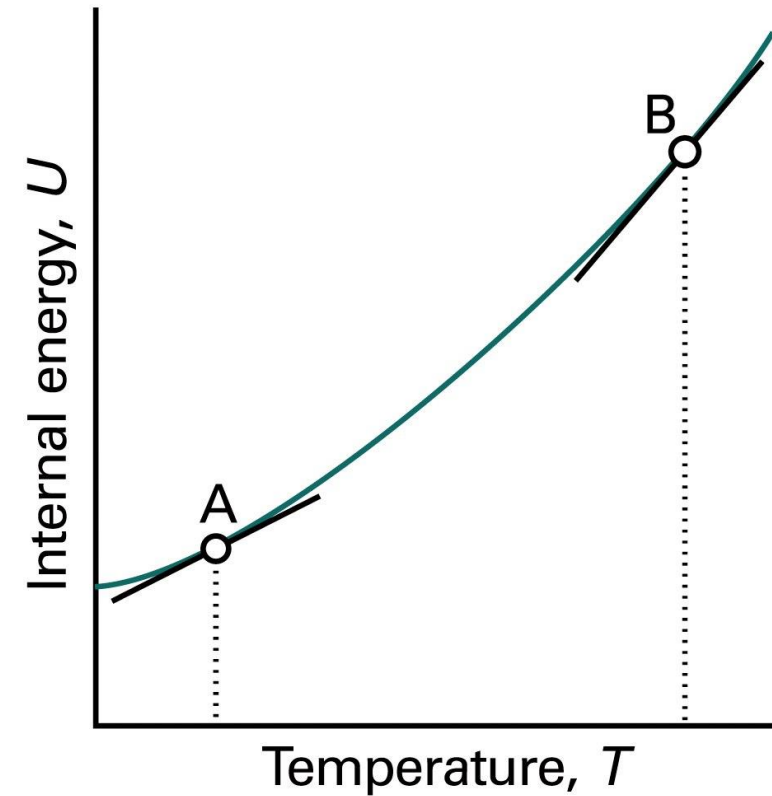

Figure 2-10
Atkins Physical Chemistry, Eighth Edition
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$$\Delta U = q + w$$

Figure 2-10
Atkins Physical Chemistry, Eighth Edition
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Temperature variation of U

Slope of U versus T at constant V

Internal energy, U

Volume, V

Temperature, T

Figure 2-11
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$$\Delta U = q + w$$

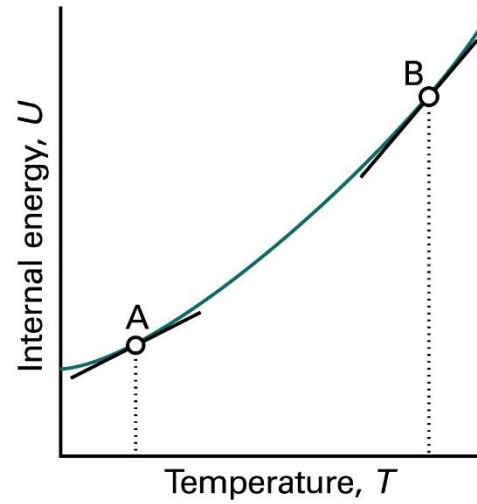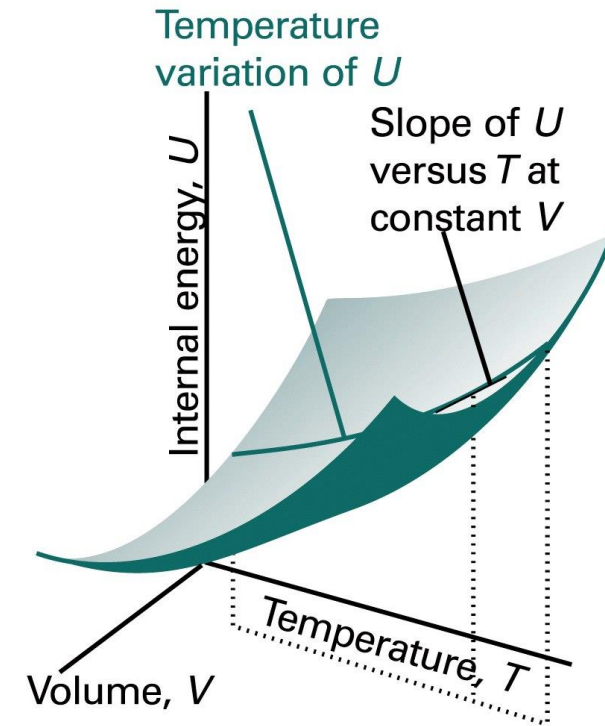$$dU = dq \quad \text{(at constant volume, no additional work)}$$

$$\Delta U = q_V$$

heat capacity at constant volume

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

Figure 2-10
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Temperature variation of U

Slope of U versus T at constant V

Internal energy, U

Volume, V

Temperature, T

Figure 2-11
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$$\Delta U = q + w$$

$\mathrm{d}U = \mathrm{d}q$ (at constant volume, no additional work)

$\Delta U = q_V$

heat capacity at constant volume

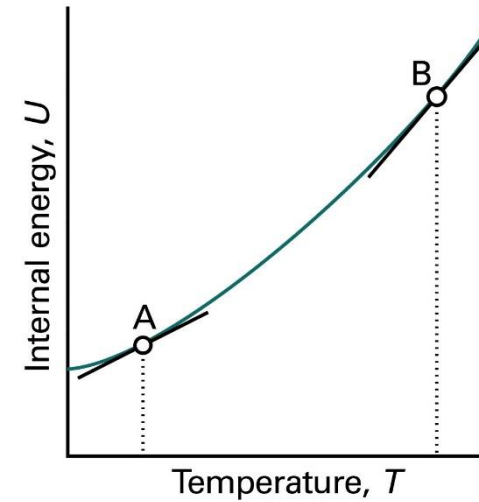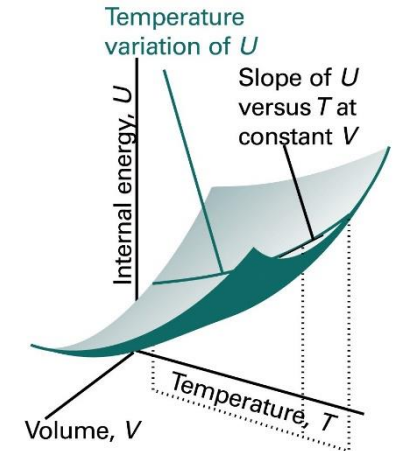$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Temperature variation of U

Slope of U versus T at constant V

Internal energy, U

Volume, V

Temperature, T

Figure 2-11
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$$q_V = C_V \Delta T$$

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

heat capacity at constant volume

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

Temperature variation of U

Slope of U versus T at constant V

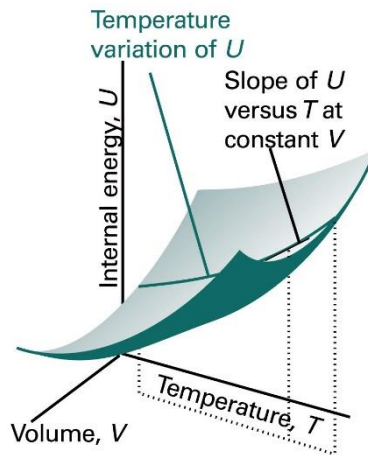Internal energy, U

Temperature, T

Volume, V

Figure 2-11
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$$\Delta U = q + w$$

$$q_V = C_V \Delta T$$

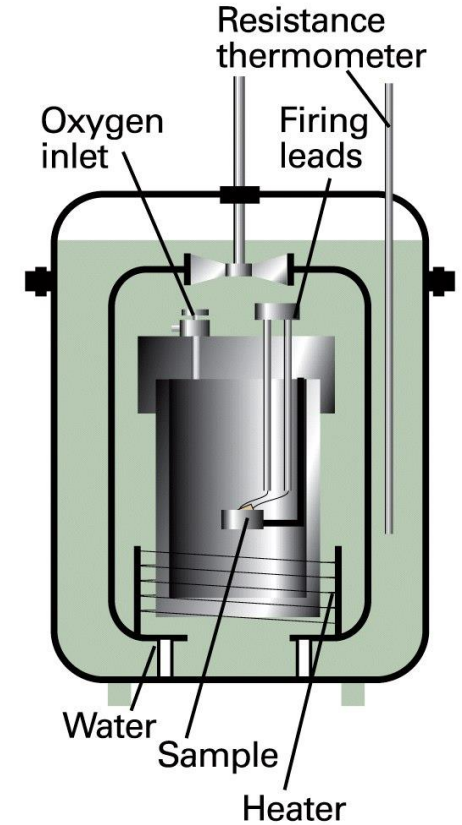$$\Delta U = C_V \Delta T \qquad \text{(at constant volume)}$$

Resistance thermometer

Oxygen inlet

Firing leads

Water

Sample

Heater

Figure 2-9
Atkins Physical Chemistry, Eighth Edition
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(a) The definition of enthalpy

The **enthalpy**, H, is defined as

$$H = U + pV$$

enthalpy is a **state function**

Energy
as work

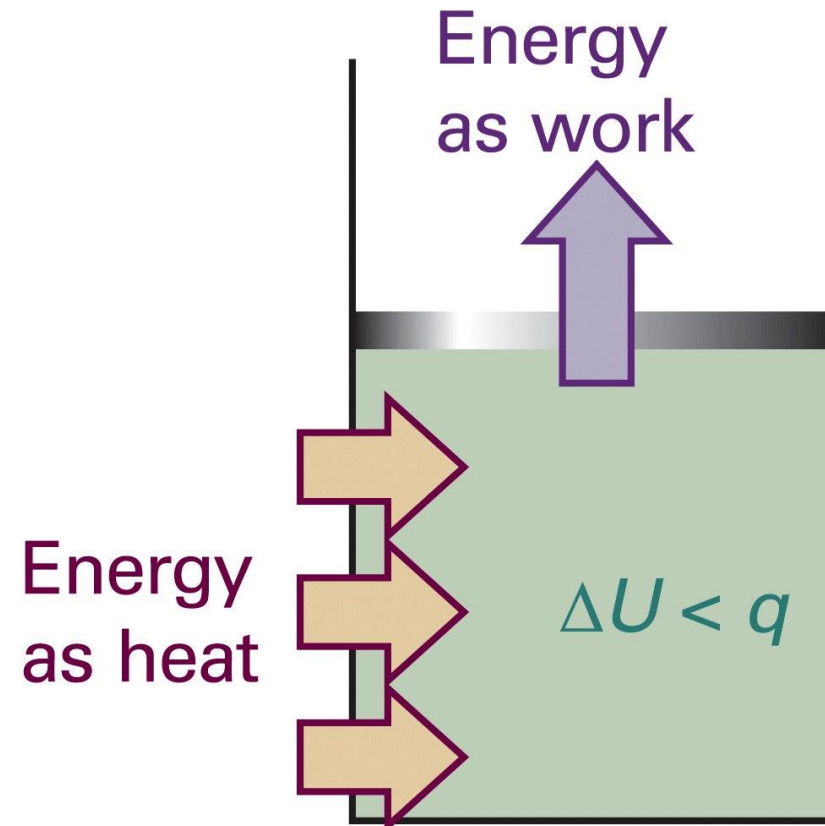Energy
as heat

$\Delta U < q$

Figure 2-12
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(a) The definition of enthalpy

The **enthalpy**, H, is defined as

$$H = U + pV$$

$$dH = dU + pdV + Vdp + dpdV$$

$$dH \cong dU + pdV + Vdp \qquad dpdV \ \dots \ very \ small$$

$$dH = dq + dw + pdV + Vdp \qquad dU = dq + dw$$

$$\qquad\qquad\qquad\qquad\qquad\qquad dU = dq - pdV$$

$$dH = dq - pdV + pdV + Vdp$$

$$\boldsymbol{dH = dq} \text{ (at constant pressure, no additional work)}$$

Energy as work
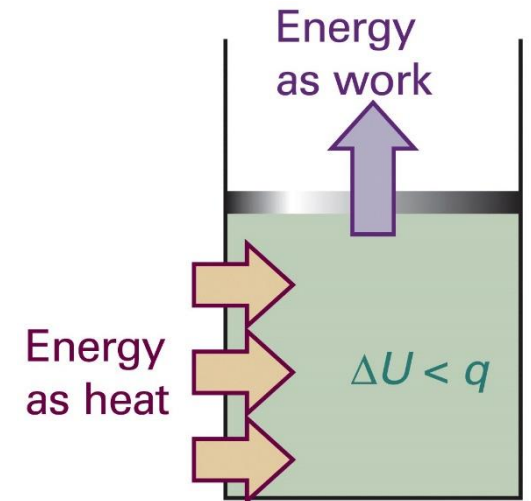
Energy as heat $\qquad \Delta U < q$

Figure 2-12
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(a) The definition of enthalpy

The **enthalpy**, H, is defined as

$$H = U + pV$$

$\mathbf{d}H = \mathbf{d}q$ (at constant pressure)

Reactions in **condensed phase**

$$H_m = U_m + pV_m \cong U_m$$

Reactions involving species in the **gaseous phase**

$$H_m = U_m + pV = U_m + nRT$$
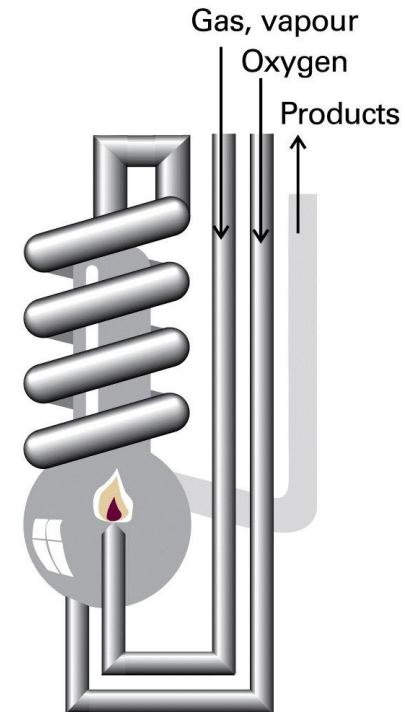
$$\Delta H = \Delta U + \Delta n_g RT$$

Gas, vapour
Oxygen
Products

Figure 2-13
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Energy
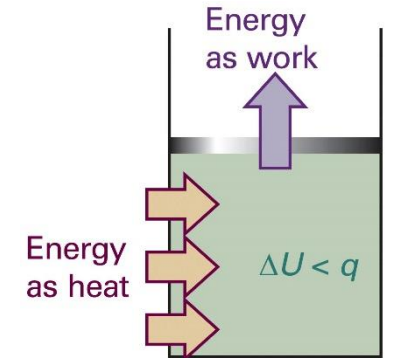as work

Energy
as heat

$\Delta U < q$

Figure 2-12
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Reactions involving species in the **gaseous phase**

$$H_\text{m} = U_\text{m} + pV = U + nRT$$

$$\Delta H = \Delta U + \Delta n_\text{g}RT$$

Gas, vapour
Oxygen
Products

Illustration 2.4 *The relation between ΔH and ΔU for gas-phase reactions*

In the reaction $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$, 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, so $\Delta n_\text{g} = -3$ mol. Therefore, at 298 K, when $RT = 2.5$ kJ mol^{-1}, the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H - \Delta U = (-3\ \text{mol}) \times RT \approx -7.4\ \text{kJ}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2.2. The enthalpy change is smaller (in this case, less negative) than the change in internal energy because, although heat escapes from the system when the reaction occurs, the system contracts when the liquid is formed, so energy is restored to it from the surroundings.
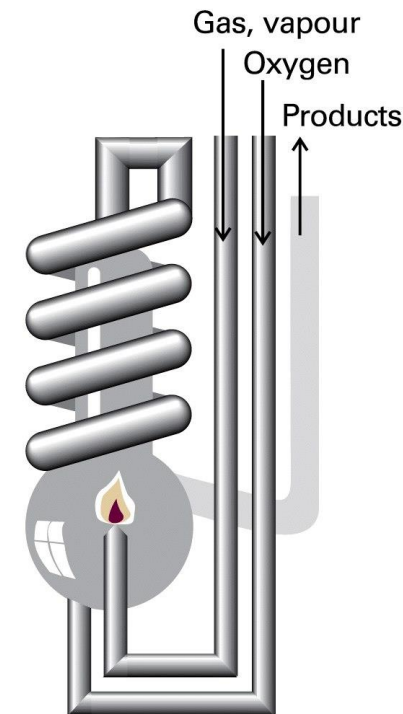
Figure 2-13
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