QF.DQB
Química-Física
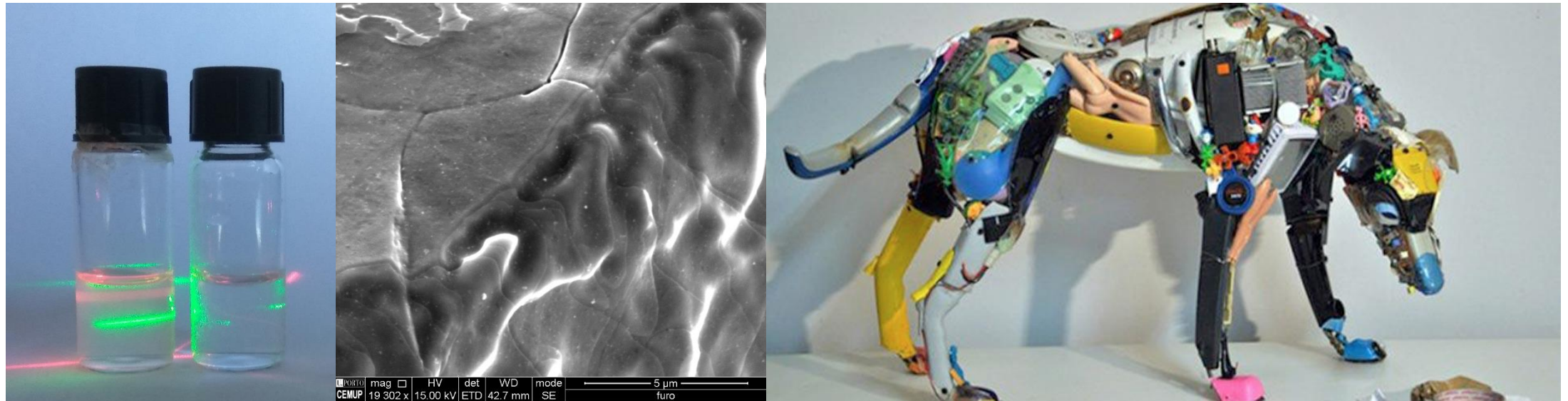Faculdade de Ciências da Universidade do Porto

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.

$$\Delta U = q + w$$

Table 2.1 Varieties of work*

Type of work	dw	Comments	Units†
Expansion	$-p_{ex}dV$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma d\sigma$	γ is the surface tension dσ is the change in area	N m^{-1} m^2
Extension	fdl	f is the tension dl is the change in length	N m
Electrical	ϕdQ	ϕ is the electric potential dQ is the change in charge	V C

* In general, the work done on a system can be expressed in the form d$w = -Fdz$, where F is a 'generalized force' and dz 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
Atkins Physical Chemistry, Eighth Edition
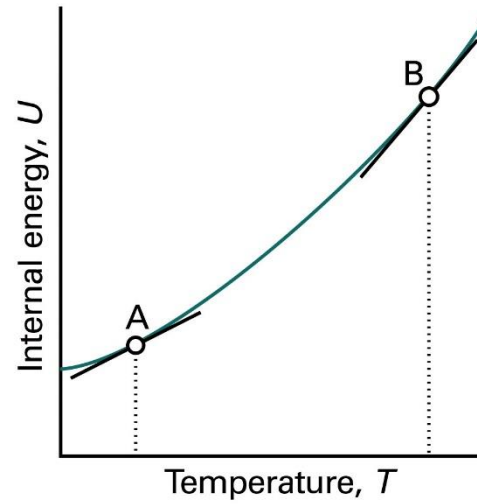© 2006 Peter Atkins and Julio de Paula

$$\Delta U = q + w$$

Figure 2-10
Atkins Physical Chemistry, Eighth Edition
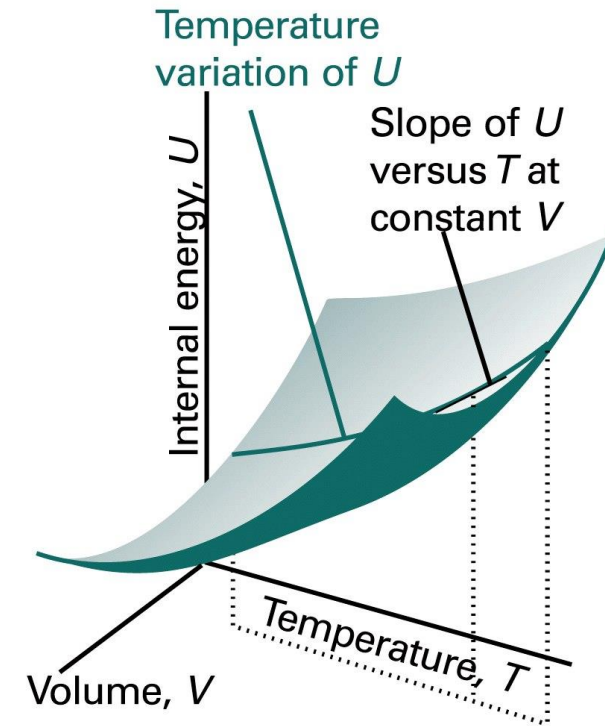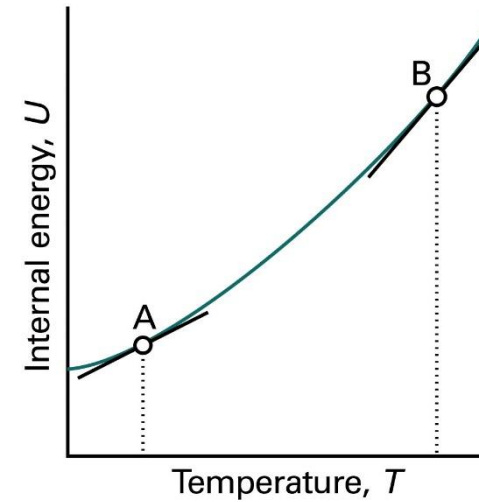© 2006 Peter Atkins and Julio de Paula

Figure 2-11
Atkins Physical Chemistry, Eighth Edition
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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*

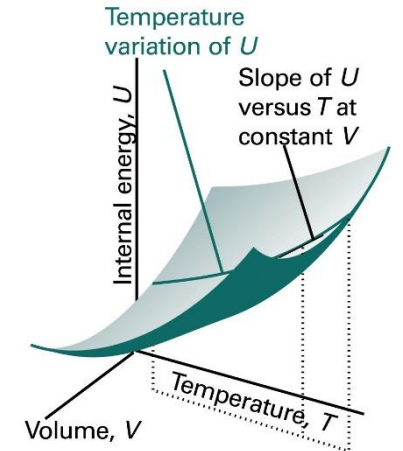Internal energy, *U*

Temperature, *T*

Volume, *V*

Figure 2-11
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Enthalpy, H

enthalpy is a **state function**

(a) The definition of enthalpy

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

$$H = U + pV$$

heat capacity at constant pressure, C_p

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

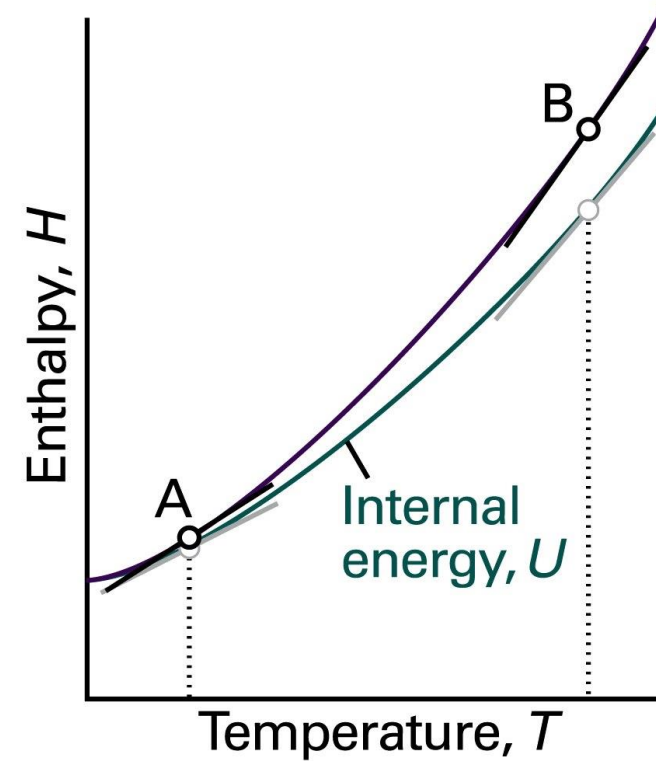$$dH = C_p dT \qquad \text{(at constant pressure)}$$

$$q_p = C_p \Delta T$$

Figure 2-14
Atkins Physical Chemistry, Eighth Edition
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enthalpy is a **state function**

heat capacity at constant pressure, $\quad C_p = \left(\dfrac{\partial H}{\partial T} \right)_p$

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

Synoptic Table 2.2* Temperature variation of molar heat capacities, $C_{p,m}/(\text{J K}^{-1}\,\text{mol}^{-1}) = a + bT + c/T^2$

	a	$b/(10^{-3}\,\text{K})$	$c/(10^5\,\text{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
$CO_2(g)$	44.22	8.79	−8.62
$H_2O(l)$	75.29	0	0
$N_2(g)$	28.58	3.77	−0.50

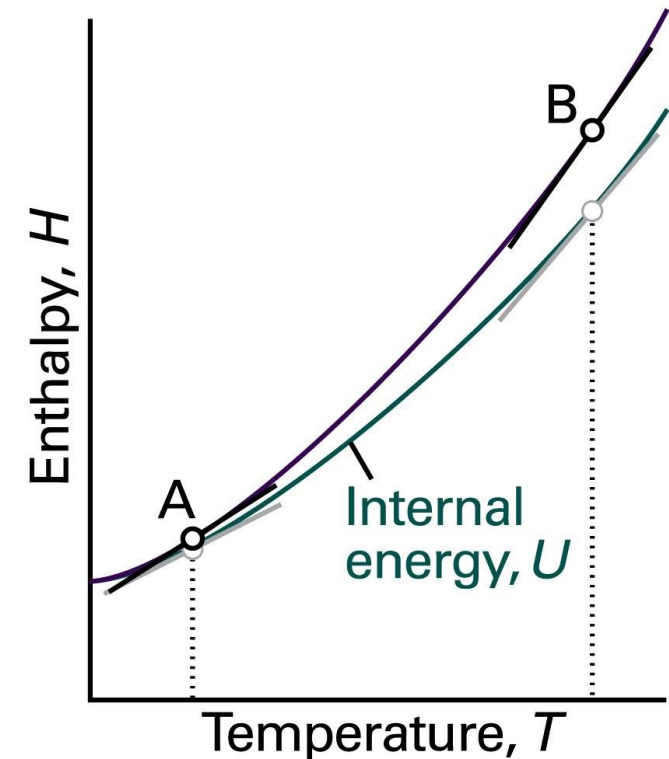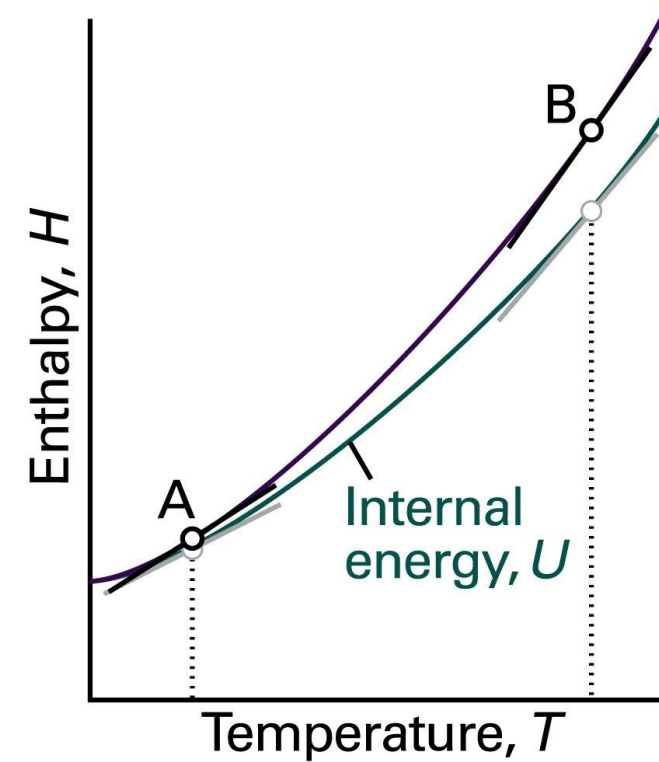* More values are given in the *Data section*.

Figure 2-14
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Enthalpy, H

enthalpy is a **state function**

heat capacity at constant pressure, $\quad C_p = \left(\dfrac{\partial H}{\partial T}\right)_P$

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

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

$$\int_{H(T_1)}^{H(T_2)} dH = \int_{T_1}^{T_2} \left(a + bT + \dfrac{c}{T^2}\right) dT$$

$$H(T_2) - H(T_1) = a(T_2 - T_1) + \tfrac{1}{2}b(T_2^2 - T_1^2) - c\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$$

Figure 2-14
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Enthalpy, H

enthalpy is a **state function**

heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$H_m \equiv U_m + pV \cong U_m + RT$$

IN GAS PHASE.. IDEAL BEHAVIOR

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = C_V = \left(\frac{\partial U}{\partial T}\right)_V + R$$
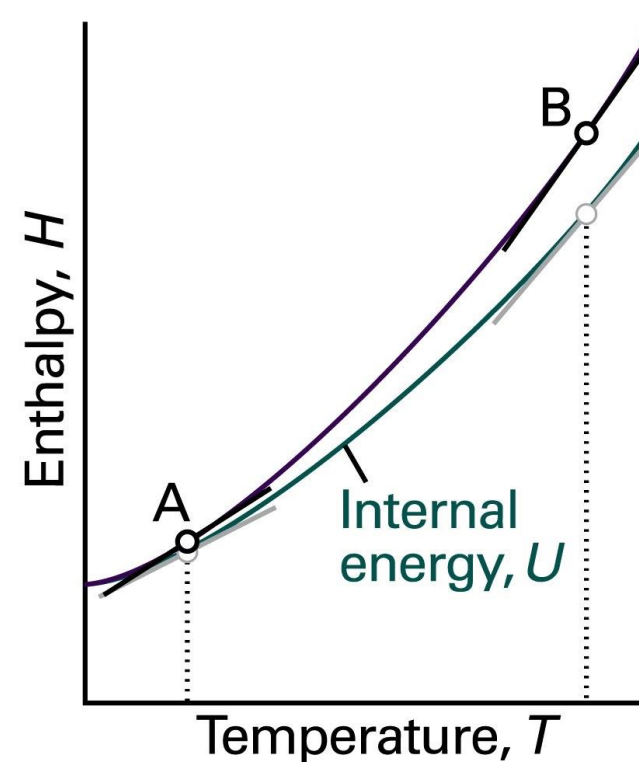
$$C_p - C_V = nR$$

Figure 2-14
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula
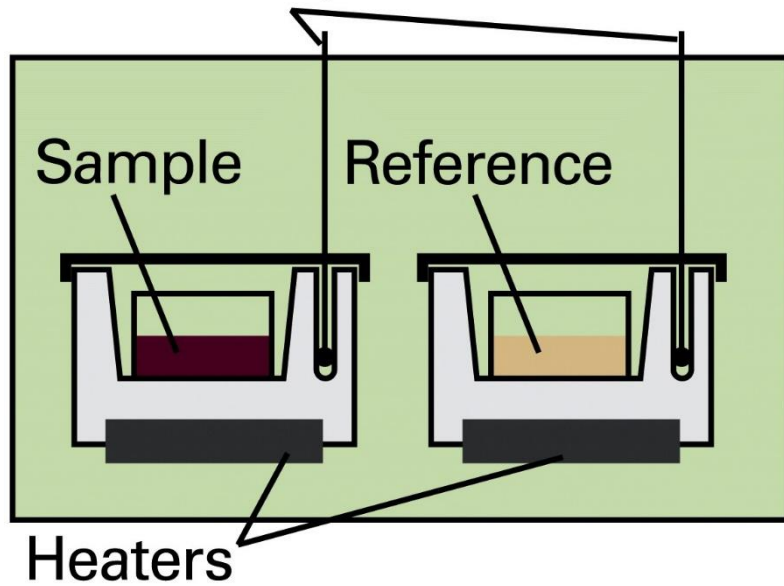
DSC - *Differential scanning calorimetry*,

Figure 2-15
Atkins Physical Chemistry, Eighth Edition
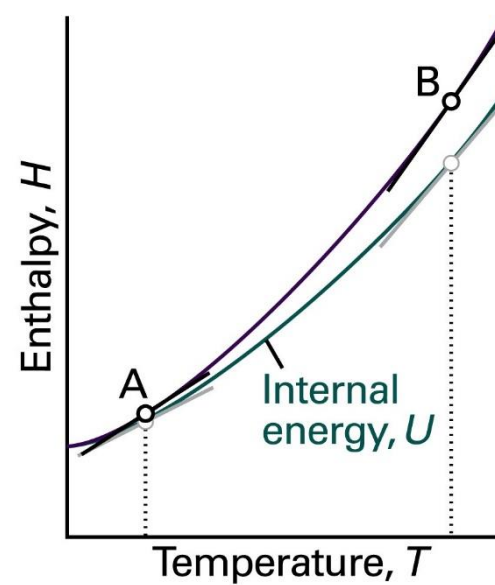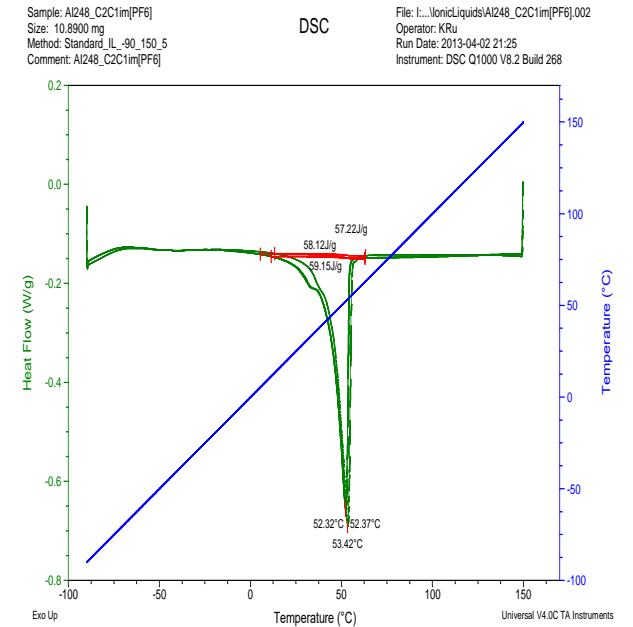© 2006 Peter Atkins and Julio de Paula

Figure 2-14
Atkins Physical Chemistry, Eighth Edition
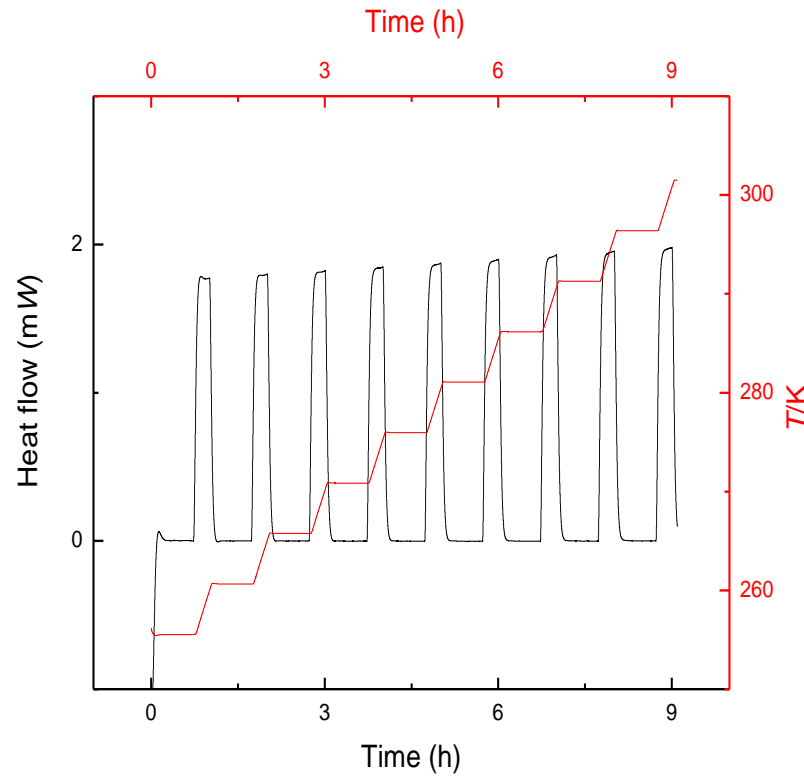© 2006 Peter Atkins and Julio de Paula

heat capacity at constant pressure,

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

Temperature step mode

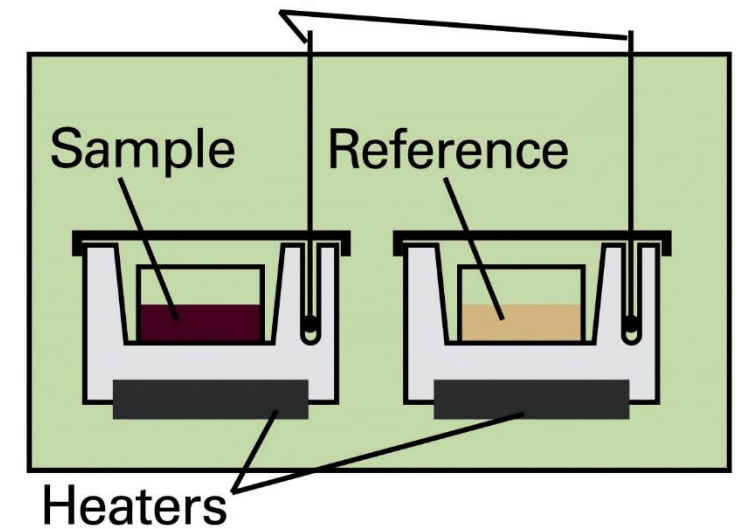$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Figure 2-15
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula
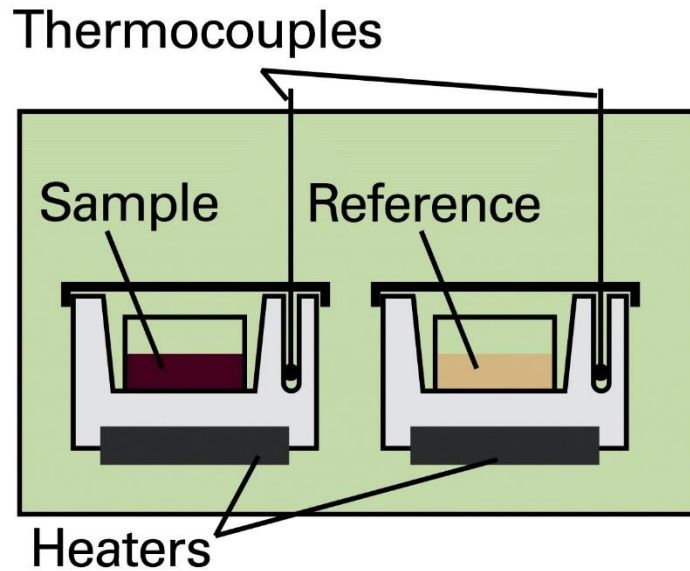
heat of a process,
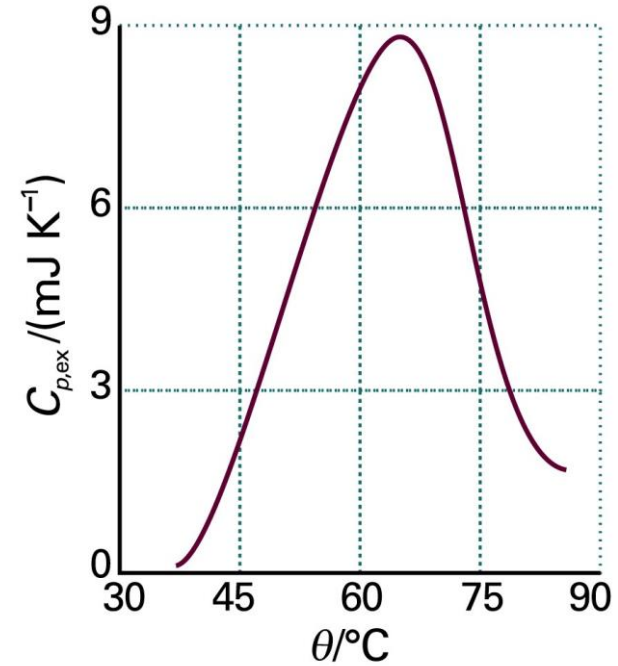"e.g. conformation change"

Figure 2-15
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Fig. 2.16 A thermogram for the protein ubiquitin at pH = 2.45. The protein retains its native structure up to about 45°C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* 74, 236 (1997).)

Figure 2-16
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U (*V*, *T*, n)
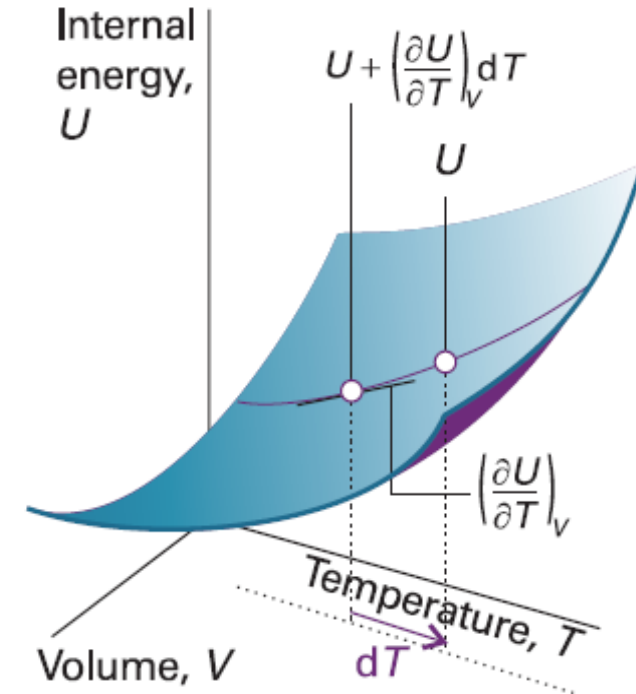
When *T* changes to $T + dT$ at constant volume

$$U' = U + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$
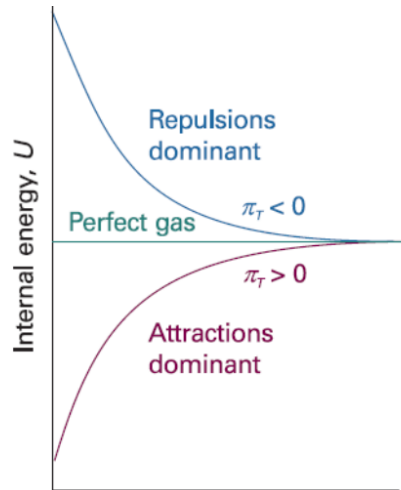
Heat capacity at constant volume

Fig. 2.22 The partial derivative $(\partial U/\partial T)_V$ is the slope of U with respect to T with the volume V held constant.

U (V, T, n)   First Law of Thermodynamics

When V changes to $V + dV$ at constant temperature
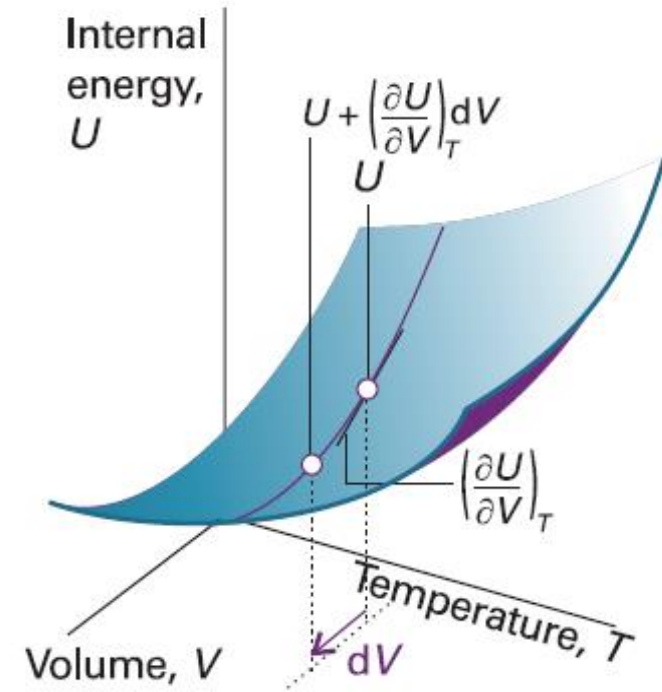
$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$ Internal pressure

$$\pi_T = 0.$$ Perfect gas

$pV=nRT$ Only depends of temperature

Internal energy, U

Repulsions dominant

$\pi_T < 0$

Perfect gas

$\pi_T > 0$

Attractions dominant

Fig. 2.21 The partial derivative $(\partial U/\partial V)_T$ is the slope of U with respect to V with the temperature T held constant.
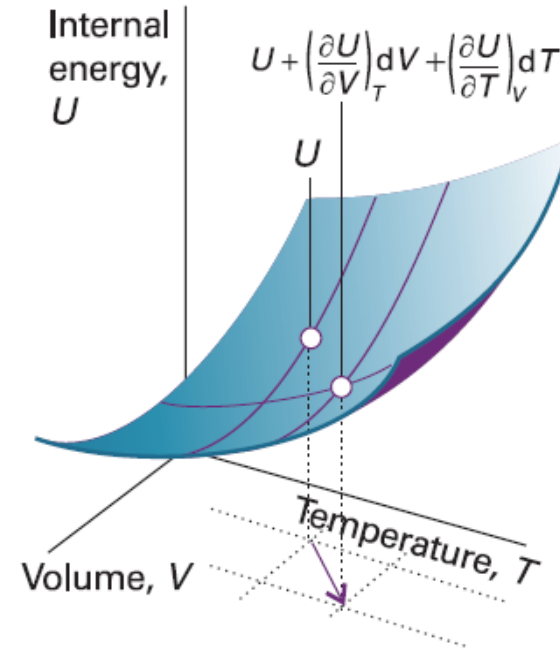
U (V, T, n)

When T and V changes to $T + dT$ and $V + dV$

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dU = \pi_T dV + C_V dT$$

$$U + \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Fig. 2.23 An overall change in U, which is denoted dU, arises when both V and T are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.
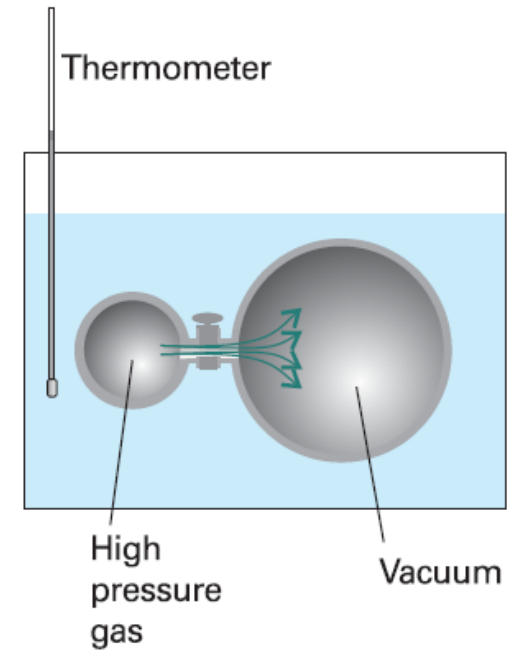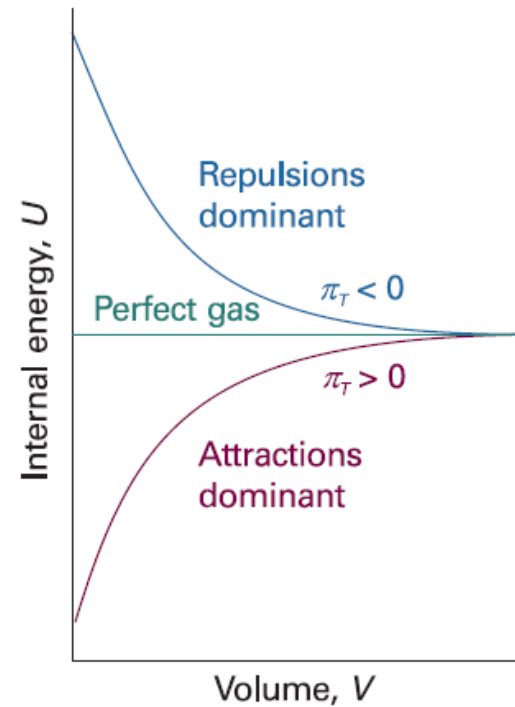
The Joule experiment

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dU = \pi_T dV + C_V dT$$

Changes in internal energy at constant pressure

$$dU = \pi_T dV + C_V dT$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \pi_T \left(\frac{\partial V}{\partial T}\right)_P + C_V$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \alpha \pi_T V + C_V$$

expansion coefficient,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

Synoptic Table 2.8* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4}\,\text{K}^{-1})$	$\kappa_T/(10^{-6}\,\text{bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

* More values are given in the *Data section*.