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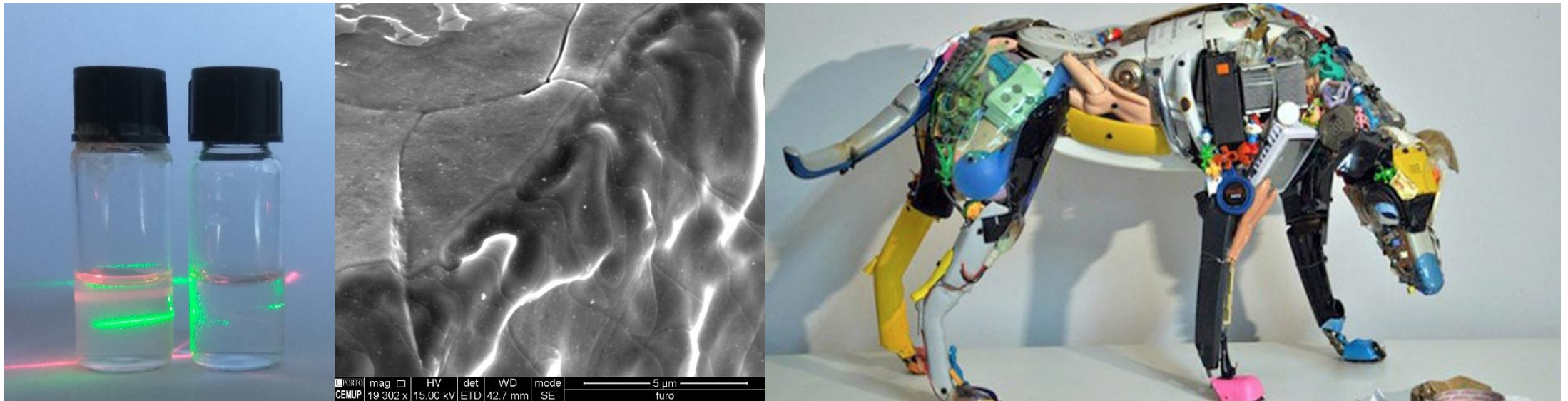Faculdade de Ciências da Universidade do Porto
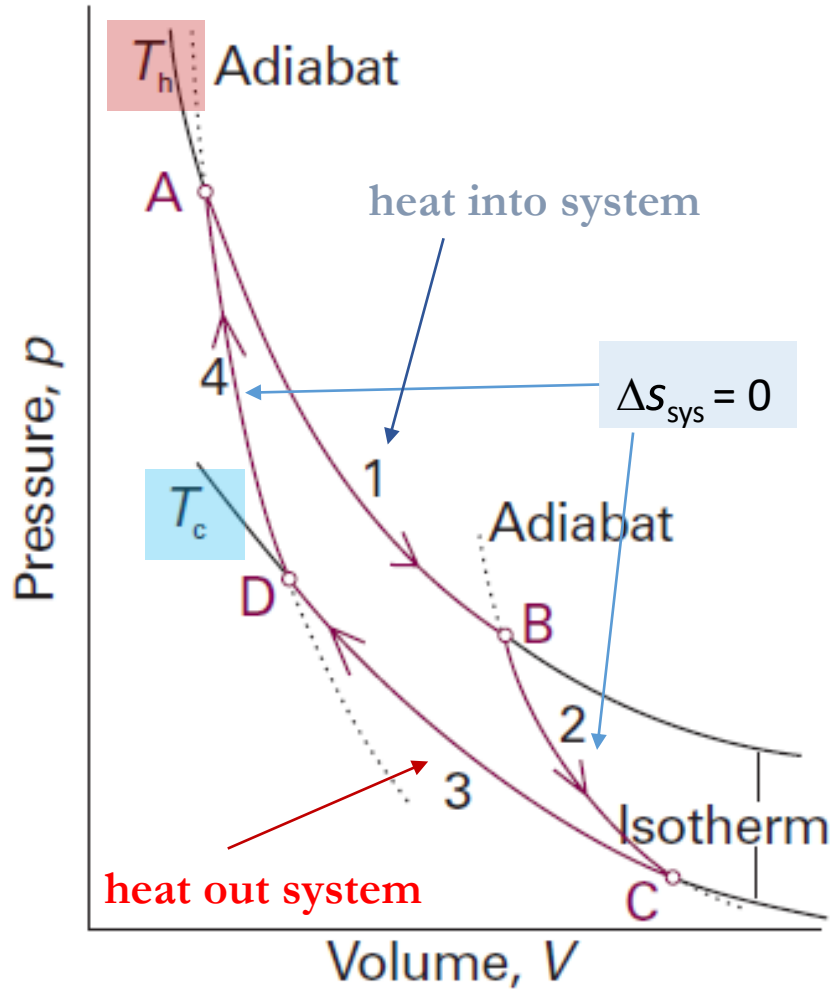
Physical Chemistry

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

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

Spontaneous Physical and Chemical Processes !!?

Carnot Cycle

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

T_h Adiabat

A

heat into system

4

$\Delta S_{sys} = 0$

1

T_c

Adiabat

D

B

2

3

Isotherm

heat out system

C

Pressure, p

Volume, V

1. Reversible isothermal expansion

Endothermic q_h $\Delta_1 S_{sys} = q_h / T_h$ S_{sys} increases

2. Reversible adiabatic expansion

$\Delta_2 S_{sys} = 0$; $\Delta S_u = 0$ **falls of** T

3. Reversible isothermal compression

Exothermic q_c $\Delta_3 S_{sys} = q_c / T_c$ S_{sys} decreases

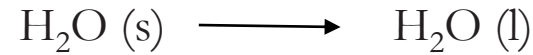**4.** Reversible adiabatic compression

$\Delta_4 S_{sys} = 0$; $\Delta S_u = 0$ **rise of** T

(b) Phase transition

At constant pressure

$q = \Delta_{trs}H,$
change in molar entropy of the system

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

$H_2O\ (s) \longrightarrow H_2O\ (l)$

$\Delta_{trs}H = 6.01\ \text{kJmol}^{-1}$

$\Delta_{trs}S = 6.01\text{x}10^3/273.15 = 22.0\ \text{JK}^{-1}\text{mol}^{-1}$

Synoptic Table 3.1* Standard entropies (and temperatures) of phase transitions, $\Delta_{trs}S^{\ominus}/(\text{J K}^{-1}\ \text{mol}^{-1})$

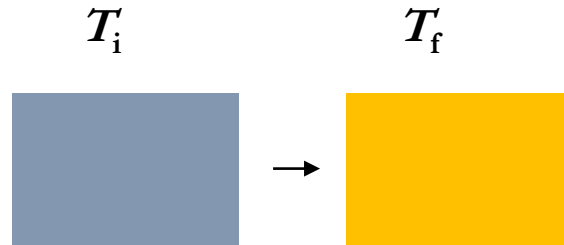|	Fusion (at T_f)	Vaporization (at T_b)
Argon, Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Benzene, C_6H_6	38.00 (at 279 K)	87.19 (at 353 K)
Water, H_2O	22.00 (at 273.15 K)	109.0 (at 373.15 K)
Helium, He	4.8 (at 8 K and 30 bar)	19.9 (at 4.22K)

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

(c) Heating

$$T_i \qquad T_f$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T}$$

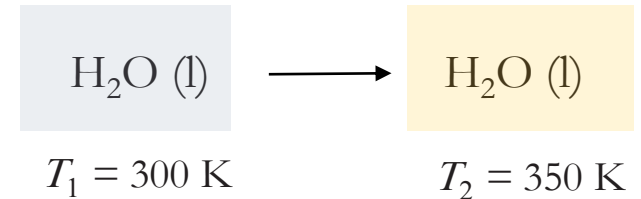If at constant pressure ..

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

The same applies at constant volume,
but with C_p replaced by C_V

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_p \ln \frac{T_f}{T_i}$$

Assuming constant C_p

$$H_2O \text{ (l)} \longrightarrow H_2O \text{ (l)}$$

$$T_1 = 300 \text{ K} \qquad T_2 = 350 \text{ K}$$

$$C_p = 4.184 \text{ JK}^{-1}\text{mol}^{-1}$$
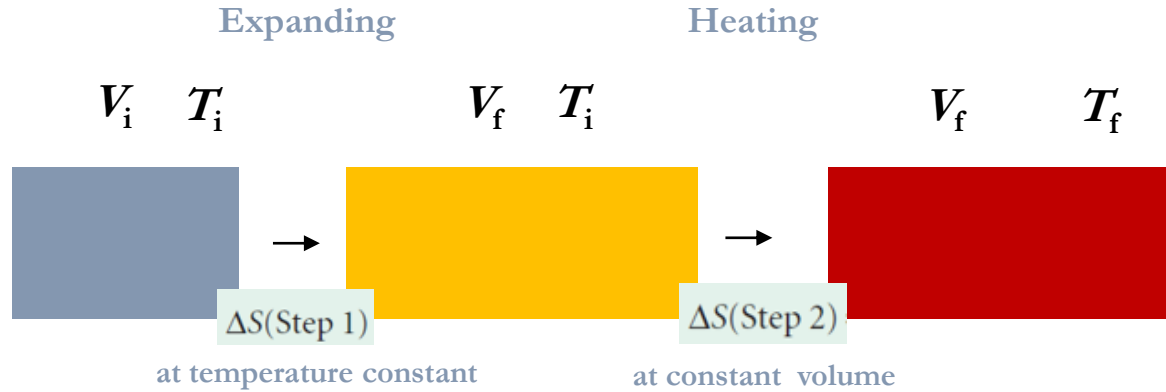
$$\Delta S = S(T_f) - S(T_i) = C_p . \ln (T_f / T_i)$$

$$\Delta S = 4.184 . \ln (350 / 300)$$

$$\Delta S = 0.6450 \text{ JK}^{-1}\text{mol}^{-1}$$

(c) Heating and expanding

Expanding   Heating

$$V_\text{i} \quad T_\text{i} \qquad\qquad V_\text{f} \quad T_\text{i} \qquad\qquad V_\text{f} \qquad T_\text{f}$$

$\Delta S(\text{Step 1})$ $\Delta S(\text{Step 2})$

at temperature constant   at constant volume

$$pV = nRT$$

$$n = pV/RT$$

Mono atomic gases

$$C_{v,m} = 3/2\ R$$

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

$$C_{p,m} = 5/2\ R$$

$$\Delta S(\text{Step 1}) = \left(\frac{p_\text{i}V_\text{i}}{RT_\text{i}}\right) \times R \ln \frac{V_\text{f}}{V_\text{i}} = \frac{p_\text{i}V_\text{i}}{T_\text{i}} \ln \frac{V_\text{f}}{V_\text{i}}$$

$$\Delta S(\text{Step 2}) = \left(\frac{p_\text{i}V_\text{i}}{RT_\text{i}}\right) \times \tfrac{3}{2}R \ln \frac{T_\text{f}}{T_\text{i}} = \frac{p_\text{i}V_\text{i}}{T_\text{i}} \ln \left(\frac{T_\text{f}}{T_\text{i}}\right)^{3/2}$$

$$\Delta S = \frac{p_\text{i}V_\text{i}}{T_\text{i}} \ln \frac{V_\text{f}}{V_\text{i}} + \frac{p_\text{i}V_\text{i}}{T_\text{i}} \ln \left(\frac{T_\text{f}}{T_\text{i}}\right)^{3/2} = \frac{p_\text{i}V_\text{i}}{T_\text{i}} \ln\left\{\frac{V_\text{f}}{V_\text{i}}\left(\frac{T_\text{f}}{T_\text{i}}\right)^{3/2}\right\}$$

overall entropy change

(c) Heating and expanding

Overall entropy change

Expanding

V_i T_i V_f T_i

Heating

V_f T_f

$\Delta S(\text{Step 1})$
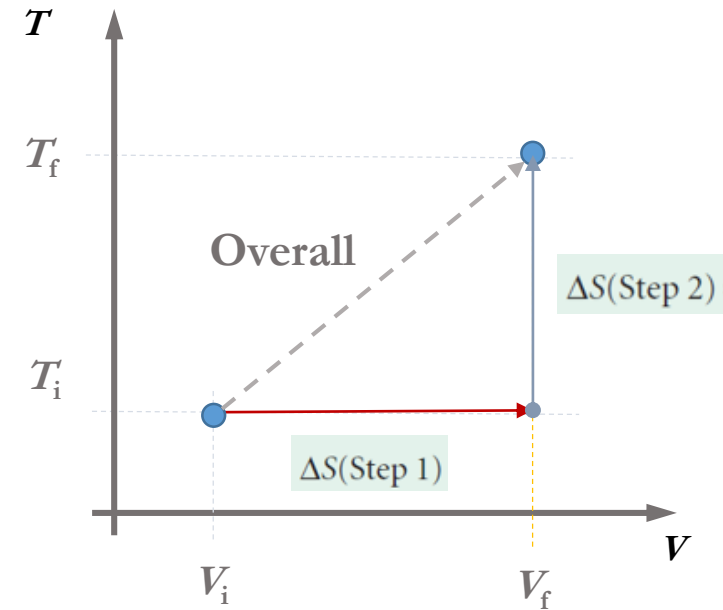
at temperature constant

$\Delta S(\text{Step 2})$

at constant volume

$$\Delta S(\text{Step 1}) = \left(\frac{p_i V_i}{R T_i}\right) \times R \ln \frac{V_f}{V_i} = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i}$$

$$\Delta S(\text{Step 2}) = \left(\frac{p_i V_i}{R T_i}\right) \times \tfrac{3}{2} R \ln \frac{T_f}{T_i} = \frac{p_i V_i}{T_i} \ln \left(\frac{T_f}{T_i}\right)^{3/2}$$
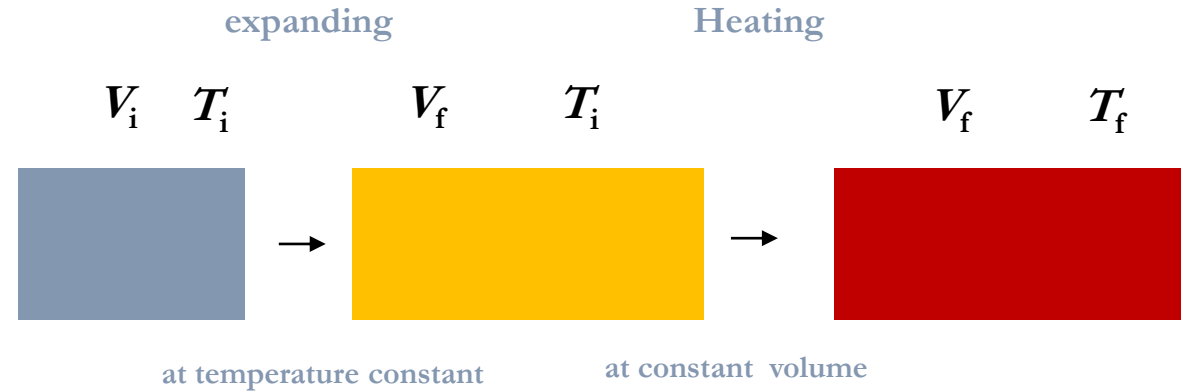
$$\Delta S = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i} + \frac{p_i V_i}{T_i} \ln \left(\frac{T_f}{T_i}\right)^{3/2} = \frac{p_i V_i}{T_i} \ln \left\{ \frac{V_f}{V_i} \left(\frac{T_f}{T_i}\right)^{3/2} \right\}$$

Entropy changes > specific processes

expanding   Heating

(c) Heating and expanding

V_i T_i V_f T_i V_f T_f

at temperature constant   at constant volume

Calculate the entropy change when argon at 25°C and 1.00 bar in a container of volume 0.500 dm³ is allowed to expand to 1.000 dm³ and is simultaneously heated to 100°C.

$$\Delta S = \frac{p_i V_i}{T_i} \ln \frac{V_f}{V_i} + \frac{p_i V_i}{T_i} \ln \left(\frac{T_f}{T_i} \right)^{3/2} = \frac{p_i V_i}{T_i} \ln \left\{ \frac{V_f}{V_i} \left(\frac{T_f}{T_i} \right)^{3/2} \right\}$$

$$\Delta S = \frac{(1.00 \times 10^5 \, \text{Pa}) \times (0.500 \times 10^{-3} \, \text{m}^3)}{298 \, \text{K}} \ln \left\{ \frac{1.000}{0.500} \left(\frac{373}{298} \right)^{3/2} \right\}$$

$$= +0.173 \, \text{J K}^{-1}$$

Entropy changes > specific processes

The measurement of entropy

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{fus}H}{T_f}$$

$$+ \int_{T_f}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_p(g)dT}{T}$$

Debye extrapolation

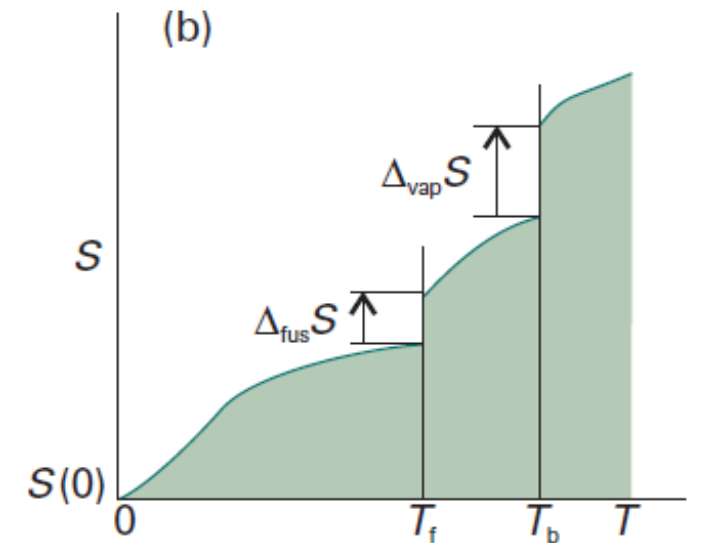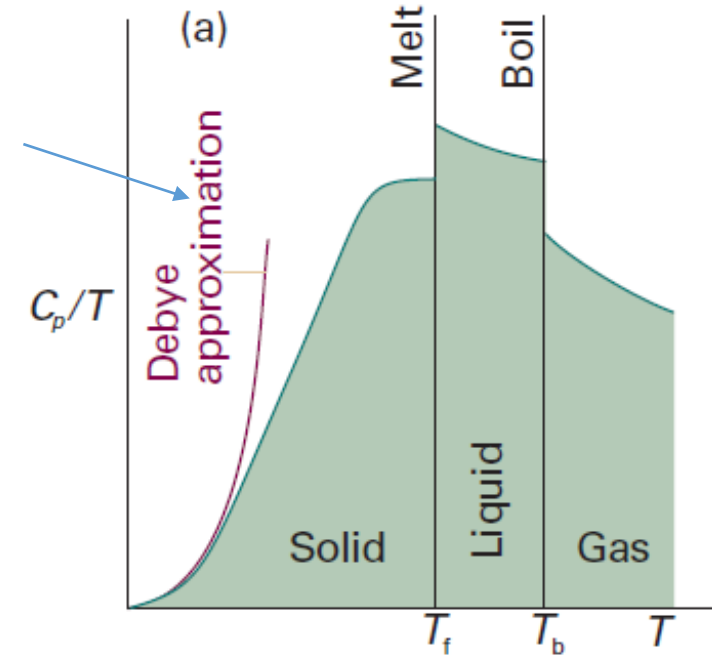$C_p = aT^3$ is assumed valid down to $T = 0$.

$C_p = aT^3$

Fig. 3.14 The calculation of entropy from heat capacity data. (a) The variation of C_p/T with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.