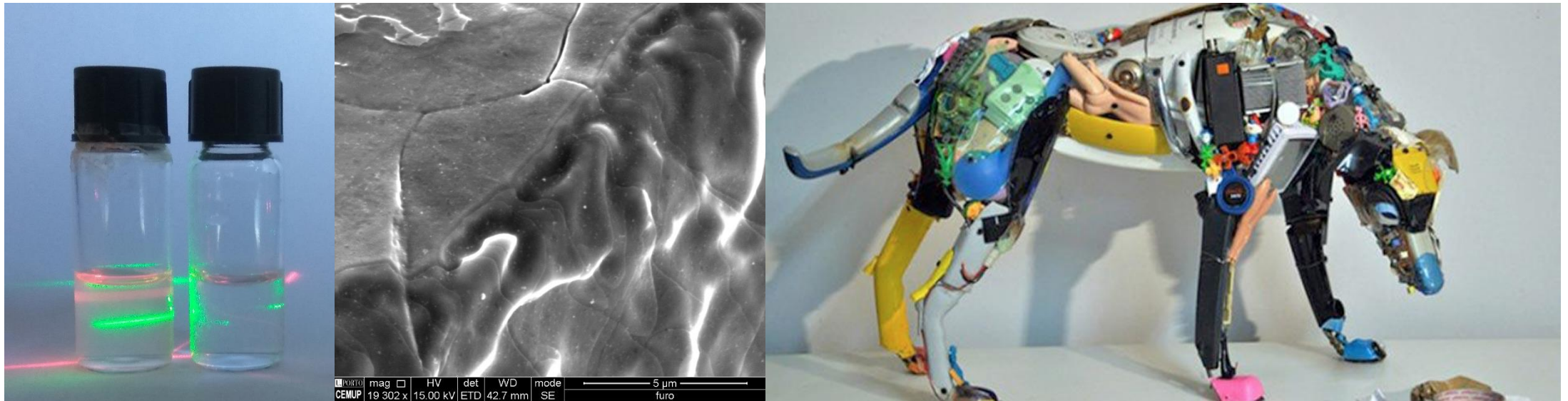# Physical Chemistry

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

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

Entropy changes > specific processes

The measurement of entropy

Debye extrapolation

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

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

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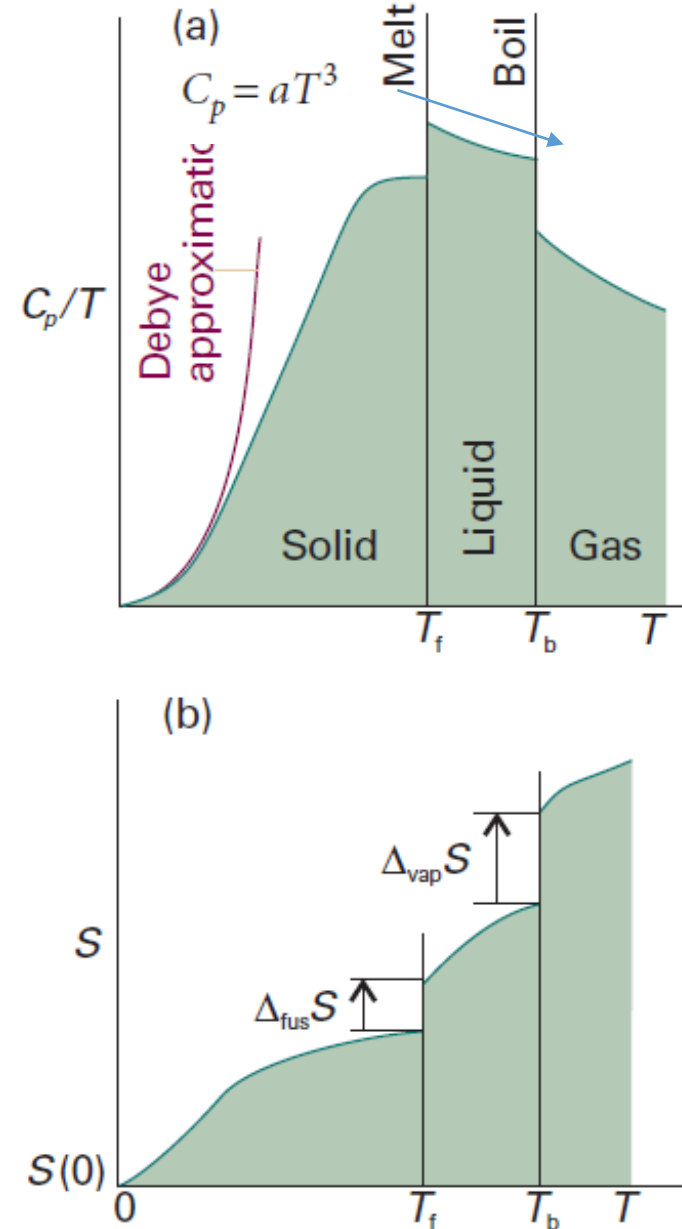

Fig. 3.14 The calculation of entropy from heat capacity data. (a) The variation of C_p/T with the temperature for a sample. (b) The entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

The measurement of entropy

Debye extrapolation

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

Example 3.3 *Calculating the entropy at low temperatures*

The molar constant-pressure heat capacity of a certain solid at 4.2 K is 0.43 J K^{-1} mol^{-1}. What is its molar entropy at that temperature?

$$S(T) = S(0) + \int_0^T \frac{aT^3 dT}{T} = S(0) + a\int_0^T T^2 dT = S(0) + \tfrac{1}{3}aT^3$$

$$S(T) = S(0) + \tfrac{1}{3}C_p(T)$$

$C_p = aT^3$

C_p/T

$T = 4.2$ K

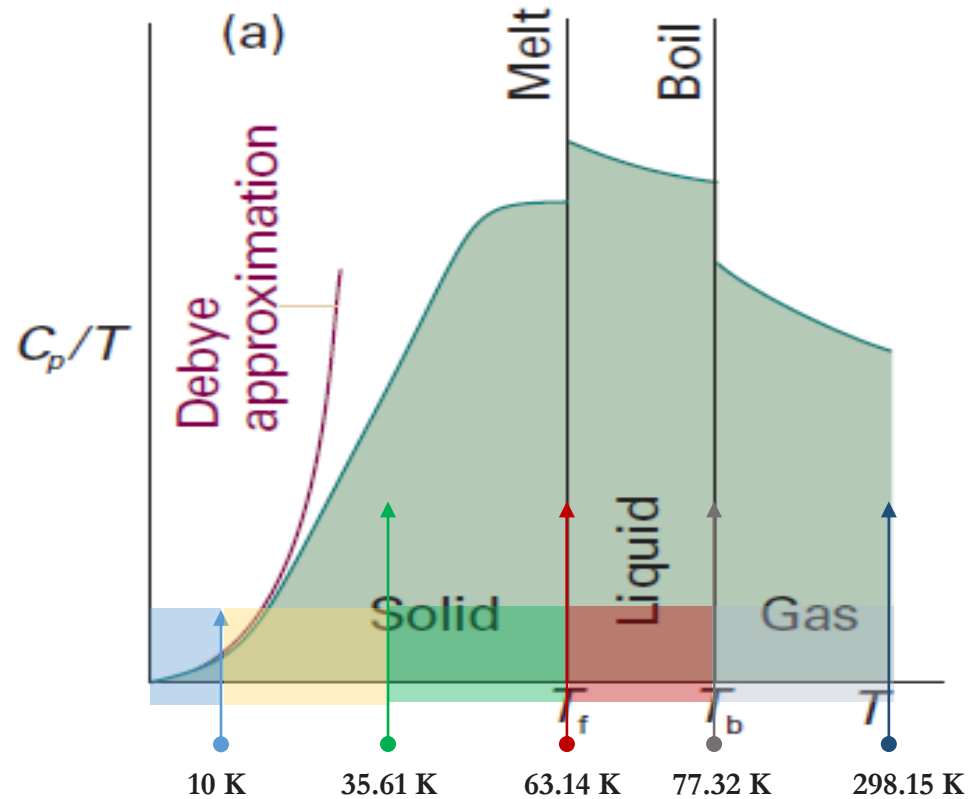$$C_p(T) = a.T^3$$

$$a = C_p(T)/T^3$$

$$a = 0.43/(4.2)^3 = 5.8 \times 10^{-3} \text{ J K}^{-4}\text{ mol}^{-1}$$

$$S_m(4.2 \text{ K}) = S_m(0\text{K}) + 1/3 . 0.43 = S_m(0\text{K}) + 0.14 \text{ J K}^{-1}\text{ mol}^{-1}$$
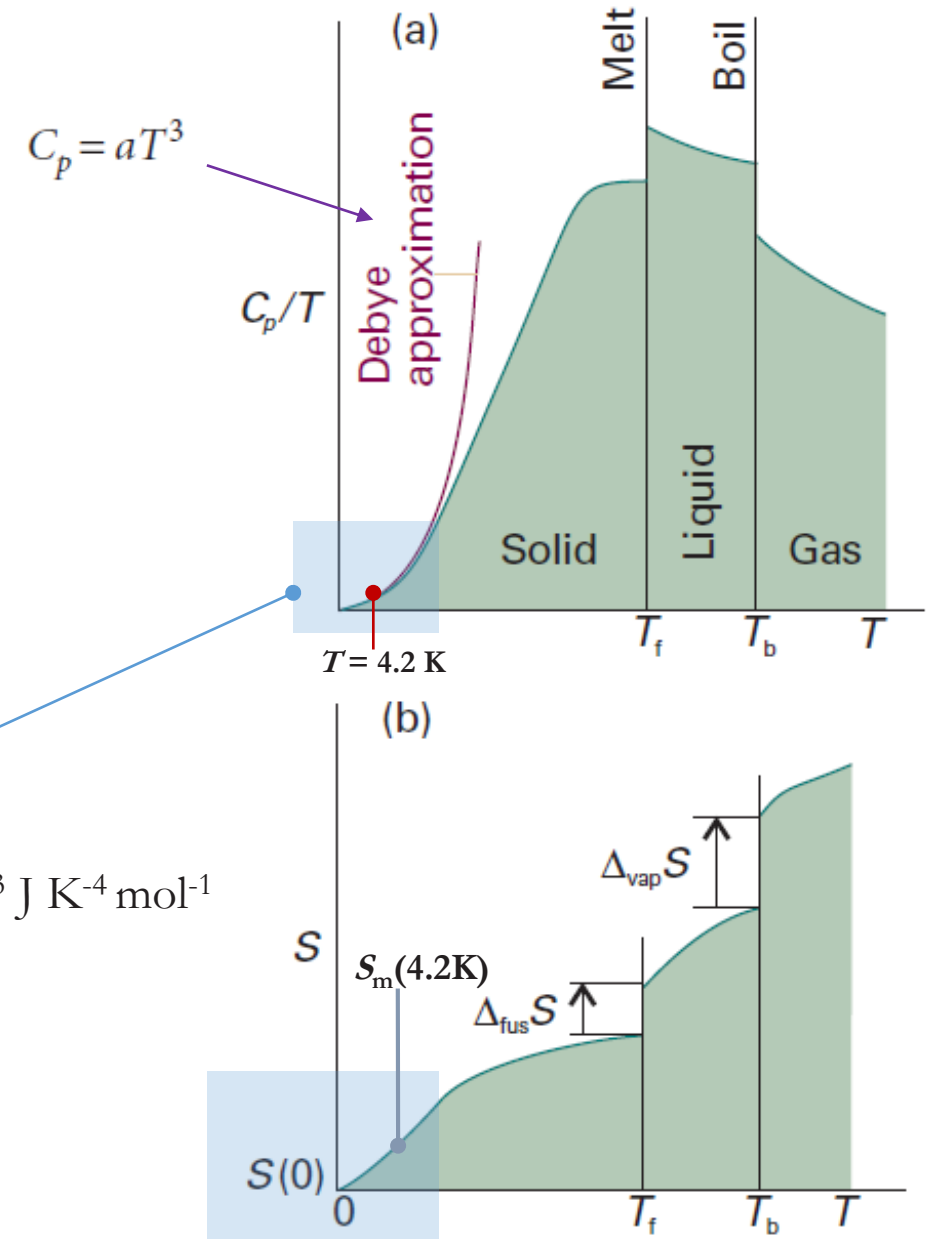
The measurement of entropy

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

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

(a)

Illustration 3.4 *Calculating a standard molar entropy*

The standard molar entropy of nitrogen gas at 25°C has been calculated from the following data:

	$S_m^{\ominus}/(\text{J K}^{-1}\text{ mol}^{-1})$
Debye extrapolation	1.92
Integration, from 10 K to 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration, from 35.61 K to 63.14 K	23.38
Fusion at 63.14 K	11.42
Integration, from 63.14 K to 77.32 K	11.41
Vaporization at 77.32 K	72.13
Integration, from 77.32 K to 298.15 K	39.20
Correction for gas imperfection	0.92
Total	192.06

Therefore,

$$S_m(298.15\text{ K}) = S_m(0) + 192.1\text{ J K}^{-1}\text{ mol}^{-1}$$

The measurement of entropy

The **Nernst** heat theorem

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly crystalline.

Illustration 3.5 *Using the Nernst heat theorem*

Consider the entropy of the transition between orthorhombic sulfur, $S(\alpha)$, and monoclinic sulfur, $S(\beta)$, which can be calculated from the transition enthalpy (-402 J mol^{-1}) at the transition temperature (369 K):

$$\Delta_{trs}S = S_m(\alpha) - S_m(\beta) = \frac{(-402 \text{ J mol}^{-1})}{369 \text{ K}} = -1.09 \text{ J K}^{-1} \text{ mol}^{-1}$$

The two individual entropies can also be determined by measuring the heat capacities from $T = 0$ up to $T = 369$ K. It is found that $S_m(\alpha) = S_m(\alpha,0) + 37$ J K^{-1} mol^{-1}

and $S_m(\beta) = S_m(\beta,0) + 38$ J K^{-1} mol^{-1}. These two values imply that at the transition temperature

$$\Delta_{trs}S = S_m(\alpha,0) - S_m(\beta,0) = -1 \text{ J K}^{-1} \text{ mol}^{-1}$$

On comparing this value with the one above, we conclude that $S_m(\alpha,0) - S_m(\beta,0) \approx 0$, in accord with the theorem.

Sulfur, S$_8$

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

Debye extrapolation

$T \rightarrow 0 \text{ K}$

$\Delta S \rightarrow 0$

$$\frac{\partial C_p}{\partial T} \rightarrow 0$$

$C_p \rightarrow 0$

Third-law of thermodynamics

The entropy of all perfect crystalline substances is zero at $T = 0$.

Entropies reported on the basis that
$$S(0) = 0 \qquad T = 0 \ K$$

Third-Law entropies

A **diatomic molecule AB** there may be almost no energy difference between the arrangements . . .

AB AB AB . . . and . . . BA AB BA . . . ,

so $W > 1$ even at $T = 0$.

If $S > 0$ at $T = 0$ we say that the substance has a **residual entropy**.

Synoptic Table 3.3* Standard Third-Law entropies at 298 K

	$S_m^{\ominus}/(J \ K^{-1} \ mol^{-1})$
Solids	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.2
Iodine, I_2(s)	116.1
Liquids	
Benzene, C_6H_6(l)	173.3
Water, H_2O(l)	69.9
Mercury, Hg(l)	76.0
Gases	
Methane, CH_4(g)	186.3
Carbon dioxide, CO_2(g)	213.7
Hydrogen, H_2(g)	130.7
Helium, He	126.2
Ammonia, NH_3(g)	126.2

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

Third-law of thermodynamics

standard reaction entropy, $\Delta_r S^{\ominus}$:

$$\Delta_r S^{\ominus} = \sum_{\text{Products}} v S_m^{\ominus} - \sum_{\text{Reactants}} v S_m^{\ominus}$$

To calculate the standard reaction entropy of $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ at 25°C, we use the data in Table 2.7 of the *Data Section* to write

$$\Delta_r S^{\ominus} = S_m^{\ominus}(H_2O, l) - \{S_m^{\ominus}(H_2, g) + \frac{1}{2} S_m^{\ominus}(O_2, g)\}$$

$$= 69.9 \text{ J K}^{-1} \text{ mol}^{-1} - \{130.7 + \frac{1}{2}(205.0)\} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -163.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

The negative value is consistent with the conversion of two gases to a compact liquid.

Synoptic Table 3.3* Standard Third-Law entropies at 298 K

	$S_m^{\ominus}/(\text{J K}^{-1}\text{mol}^{-1})$
Solids	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.2
Iodine, I_2(s)	116.1
Liquids	
Benzene, C_6H_6(l)	173.3
Water, H_2O(l)	69.9
Mercury, Hg(l)	76.0
Gases	
Methane, CH_4(g)	186.3
Carbon dioxide, CO_2(g)	213.7
Hydrogen, H_2(g)	130.7
Helium, He	126.2
Ammonia, NH_3(g)	126.2

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

Third-law of thermodynamics

standard reaction entropy, $\Delta_r S^\ominus$,

$$\Delta_r S^\ominus = \sum_{\text{Products}} v S_m^\ominus - \sum_{\text{Reactants}} v S_m^\ominus$$

the H^+ ions in water is taken as zero at all temperatures:

$$S^\ominus(H^+, aq) = 0$$

Because the entropies of ions in water are values relative to the hydrogen ion in water, they may be either positive or negative

e.g. the standard molar entropy of

$Cl^-(aq)$ is $+57 \text{ J K}^{-1} \text{mol}^{-1}$
$Mg^{2+}(aq)$ is $-128 \text{ J K}^{-1} \text{mol}^{-1}$.

Third-law of thermodynamics

standard reaction entropy, $\Delta_r S^\ominus$: $\qquad \Delta_r S^\ominus = \sum\limits_{Products} v S_m^\ominus - \sum\limits_{Reactants} v S_m^\ominus$

e.g. **Haber process** for the production of ammonia from nitrogen and hydrogen gas

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
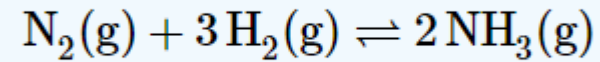
At 298.15 K :

$S^\circ\,(NH_3) = 192.5\ \ J\cdot K^{-1}\cdot mol^{-1}$

$S^\circ\,(H_2) = 130.6\ \ J\cdot K^{-1}\cdot mol^{-1}$

$S^\circ\,(N_2) = 191.5\ \ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta S^0 = 2*S^0(NH_3) - [S^0(N_2) + (3*S^0(H_2))]$

$\Delta S^0 = 2*192.5 - [191.5 + (3*130.6)]$

$\Delta S^0 =$ **-198.3** $J\cdot K^{-1}\cdot mol^{-1}$

Third-law of thermodynamics

standard reaction entropy, $\Delta_r S^{\ominus}$:

$$\Delta_r S^{\ominus} = \sum_{\text{Products}} v S_m^{\ominus} - \sum_{\text{Reactants}} v S_m^{\ominus}$$

combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(g)$$
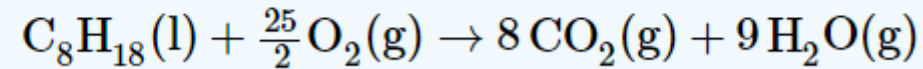
$$\Delta S_{rxn}^{\circ} = \sum m S^{\circ}(\text{products}) - \sum n S^{\circ}(\text{reactants})$$

$$= [8 S^{\circ}(CO_2) + 9 S^{\circ}(H_2O)] - [S^{\circ}(C_8H_{18}) + \frac{25}{2}S^{\circ}(O_2)]$$

$$= \{[8 \text{ mol } CO_2 \times 213.8 \text{ J/(mol} \cdot \text{K)}] + [9 \text{ mol } H_2O \times 188.8 \text{ J/(mol} \cdot \text{K)}]\}$$

$$- \left\{[1 \text{ mol } C_8H_{18} \times 329.3 \text{ J/(mol} \cdot \text{K)}] + \left[\frac{25}{2} \text{ mol } O_2 \times 205.2 \text{ J/(mol} \cdot \text{K)}\right]\right\}$$

$$= 515.3 \text{ J/K}$$