9/14/01

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* SKIP CARNOT CYCLE *

xing
eck
of
cards

ENTROPY – A MEASURE OF DISORDER

\# of microscopic states of a system = N
= # ways of arranging the components of the system

State Function

$$S = k \ln N$$

<u>2ND LAW</u> – Entropy of <u>universe</u> always increasing

$$\Delta S\ (\text{system}) + \Delta S\ (\text{surroundings}) \geq 0$$

Or if no exchange (isolated) $\Delta S_{isolated} \geq 0$

$$dS = \frac{dq_{REV}}{T}$$ ← heat xfer over a reversible path

$$\Delta S = \frac{q_{REV}}{T} \qquad \Delta S \neq \frac{q_{irrev}}{T}$$

Remember that $dq = C\,dT$

$$dS = C\frac{dT}{T}$$

$$\Delta S = C_p \int \frac{dT}{T} = C \ln T_2/T_1$$

<u>3RD LAW</u> Entropy of any pure, perfect crystal is zero at 0K

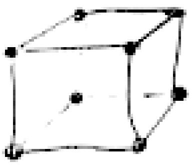
Perfect order
No disorder

No motion
Motion is disorder

Can move impurity around

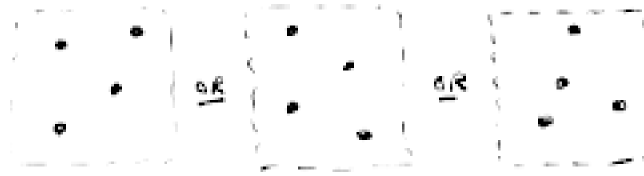
imperfection is disorder
move the imperfection around

Solid crystal



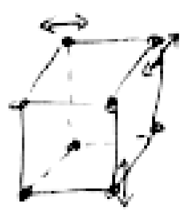
One way of arranging (at 0K)

Liquid



More ways of arranging
$\Rightarrow$ More entropy

At $T>0$



Thermal vibrations provide disorder

More as $T\uparrow$

Molar entropies of water

H_2O (s)	41.0	J/K*
H_2O (ℓ)	63.2	J/K*
H_2O (g)	188.3	J/K**

all at 0°C
P = 1 atm

$\uparrow$ (mol^{-1})

Liquid state more like solid, than like gas. $\Rightarrow$ Order in a liquid.

P = 1 atm
T = 25°C

Carbon (diamond)	2.4 J/K	<u>very</u> ordered
Carbon (graphite)	5.7 J/K	not <u>as</u> ordered

<u>Entropy of gas-involved</u> reactions simple:

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g)$$

Q: Entropy increase or decrease?
(3→2)

Not so easy to predict for liquid solutions

$J\,K^{-1}\,mol^{-1}$

OK? $2 \to 1$ $\quad CO_3^{2-}(aq) + H^+(aq) \longrightarrow HCO_3^-(aq) \quad \Delta S^\circ = +14$

Huh? $2 \to 3$ $\quad NH_4^+(aq) + HCO_3^-(aq) \rightarrow CO_2(aq) + H_2O(l) + NH_3(aq) \quad \Delta S^\circ = +94$

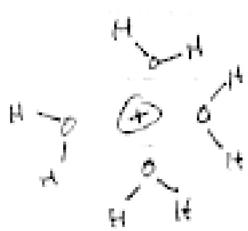
$2 \to 2$ $\quad HC_2O_4^-(aq) + OH^-(aq) \longrightarrow C_2O_4^{2-}(aq) + H_2O(l) \quad \Delta S^\circ = -23$

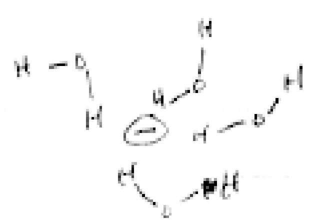
Q: Why?

A: Solvent interactions are different for products vs. reactants.

Any measured ΔS° contains solvent, so that the system is solutes + solvent.

$$\underbrace{NH_4^+(aq)}_{\text{plus ordered water}} + \underbrace{HCO_3^-(aq)}_{\text{plus ordered water}} \longrightarrow \underbrace{CO_2(aq) + H_2O(l) + NH_3(aq)}_{\text{Neutral, less water ordering needed}}$$





Remember → water has a dipole moment

$\Delta S_{rev} = \Delta S_{irrev}$ <u>IF</u> initial and final states are the same.

→ Why? ΔS is a state function.

$$\Delta S = \int_{T_1}^{T_2} \frac{q_{REV}}{T}$$

Interesting...

$$\Delta S > \int_{T_1}^{T_2} \frac{q_{irrev}}{T}$$

Calculating ΔS° using $\bar{S}_A$ $\bar{S}_B$ for reactants and $\bar{S}_C$ $\bar{S}_D$ for products

$n_a A + B \rightleftharpoons C + D$

$$\Delta S^\circ = \bar{S}_C + \bar{S}_D - (n_a\bar{S}_A + \bar{S}_B)$$

$\bar{S}^\circ$ ↑ Standard Molar Entropy $p = 1$ atm, $T = 25°C$

Same as for ΔH°.

<u>Remember</u> (page 1 today)

At const P_1: $\Delta S = \int_{T_1}^{T_2} \frac{C_p\, dT}{T}$

<u>As before</u>:

$$\begin{array}{ccc} A(T_2) & \xrightarrow{\Delta S^\circ(T_2)} & B(T_2) \\ \downarrow & & \uparrow \\ A(25°C) & \longrightarrow & B(25°C) \end{array}$$

$$\int^{298} C_p(A)\frac{dT}{T} + \Delta S^\circ(25°C) + \int_{298}^{T} C_p(B)\frac{dT}{T}$$