The spontaneity of chemical reactions

Atkins, Chapter 4

Reaction: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

$$\Delta_r S^{\ominus} = \Sigma \nu\ S_m^{\ominus}\ \text{(products)} - \Sigma \nu\ S_m^{\ominus}\ \text{(reactants)}$$

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

$= -\ 317\ J\ K^{-1}\ mol^{-1}$

Would not be spontaneous!?

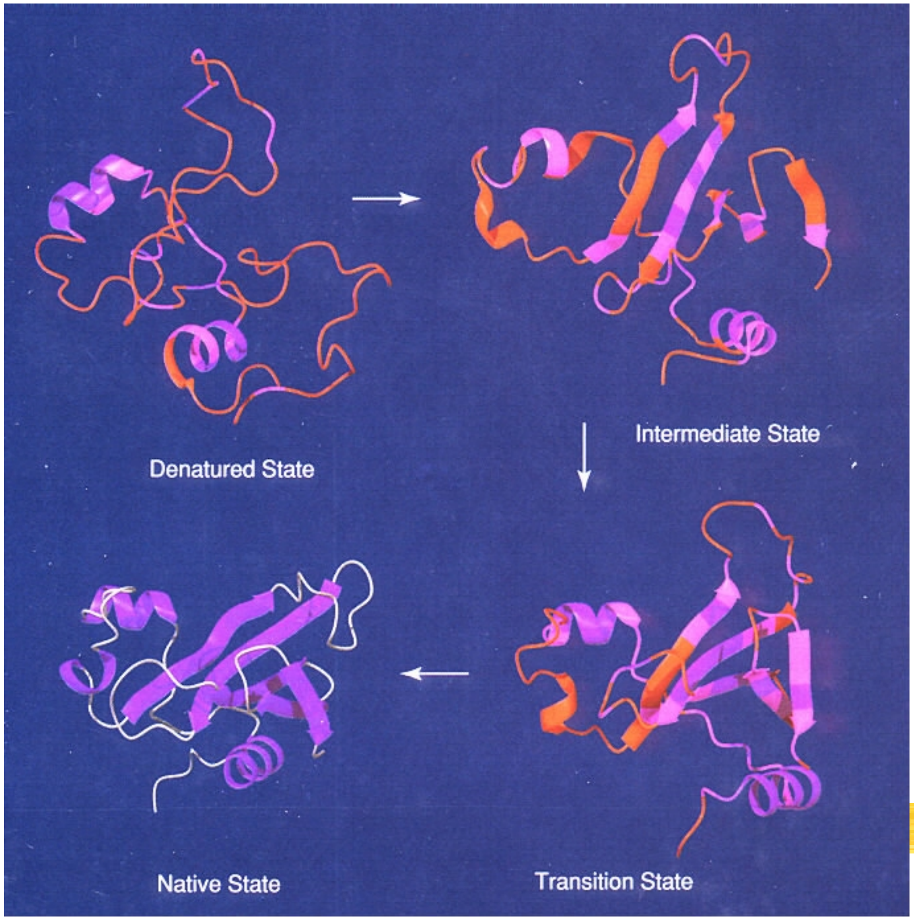
But... $$\Delta_r S_{Surr} = -\frac{\Delta_r H}{T} = -\frac{-572\ kJ\ mol^{-1}}{298\ K} = +1920\ J\ K^{-1}\ mol^{-1}$$

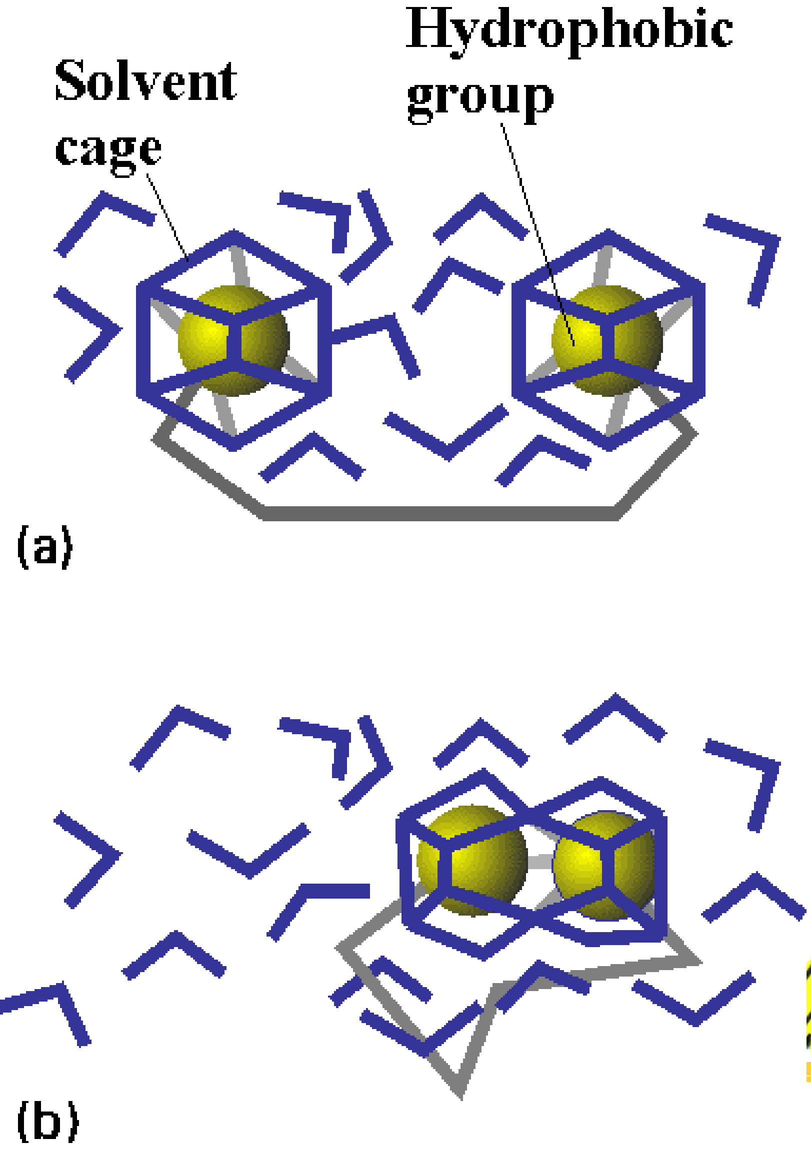
$$\Rightarrow \Delta_r S_{Univ} = \Delta_r S_{Sys} + \Delta_r S_{Surr} = +1590\ J\ K^{-1}\ mol^{-1}$$

Is spontaneous!!!

The hydrophobic effect: Water entropy drives protein folding

The hydrophobic side chains of a protein collapse on the way to the functional native structure





The Gibbs free enthalpy ("Gibbs energy")

To judge whether a chemical reaction is spontaneous, we need to consider entropy changes in both system and surroundings

$$\Delta S_{Univ} = \Delta S_{Sys} + \Delta S_{Surr} = \Delta S_{Sys} - \frac{\Delta H}{T}$$ (@ constant p, T)

⇒ Josiah Willard Gibbs (1839-1903; theoretician @ Yale):

Definition: $G = H - TS$

H, S are extensive
⇒ G is extensive
(increases with n)

all state functions
⇒ G is a state function
(no memory of path)

⇒ change in G: $\Delta G = \Delta H - T\,\Delta S = -T\,\Delta S_{Univ}$ (@ constant p, T)

⇒ The Gibbs free enthalpy calculates changes in entropy of both system and surroundings from system parameters alone

Spontaneity

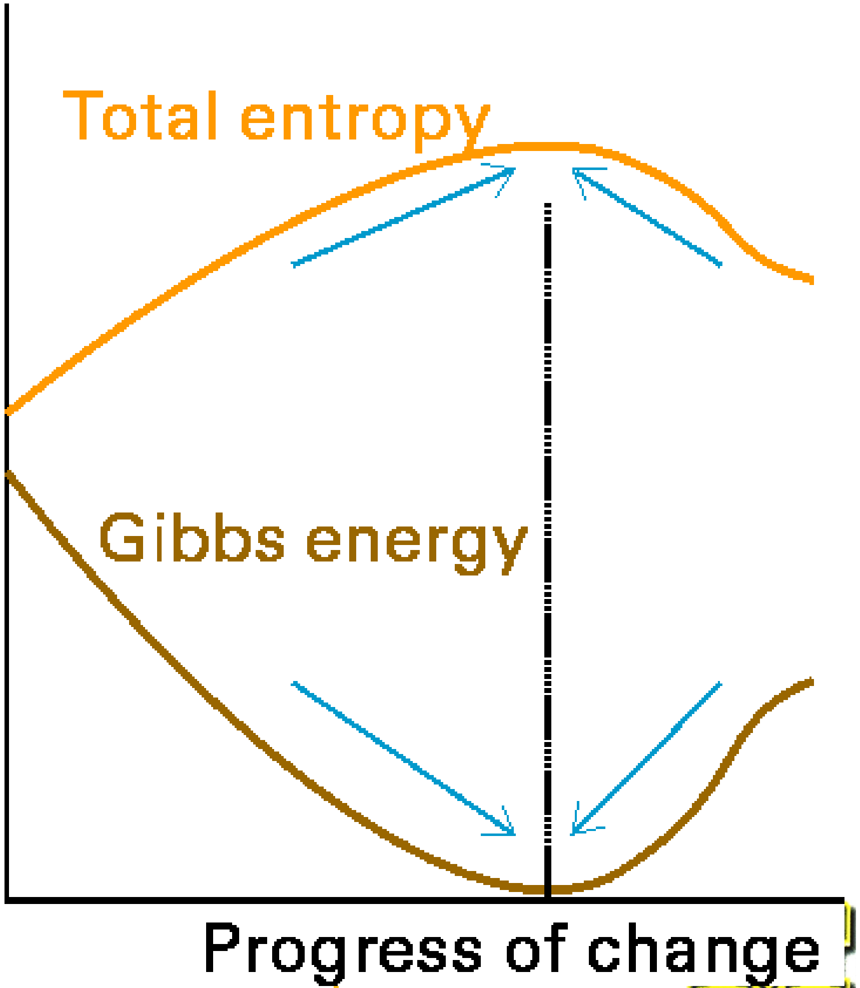
$\Delta G = \Delta H - T\,\Delta S = -T\,\Delta S_{Univ}$ (@ constant p, T)

2nd law of thermodynamics:

$\Delta S_{Univ} \geq 0$ (J K^{-1})

$\Rightarrow \Delta G \leq 0$ (J) (@ constant p, T)

> **"In a spontaneous change at constant temperature and pressure, the Gibbs energy decreases"**



ΔG describes the maximum non-expansion work @ constant p, T

infinitesimal changes of G: $dG = dH - TdS$ (2nd law)

and $dH = dU + pdV$ (@ constant p)

$\Rightarrow dG = dU + pdV - TdS$

and $dU = dw + dq$ (1st law)

$\Rightarrow dG = dw + dq + pdV - TdS$

and $dw = \boxed{-p_{ex}dV} + \boxed{dw'}$

expansion work

non-expansion work

$\Rightarrow dG = \cancel{-p_{ex}dV} + dw' + \cancel{dq} + \cancel{pdV} - \cancel{TdS}$

For reversible changes: $p = p_{ex}$ and $dq = TdS$

$\Rightarrow dG = dw'_{rev} = dw'_{max}$; overall: $\Delta G = w'_{max}$

Meaning of the Gibbs energy

Atkins: “If we know ΔG of a reaction, then we know the maximum non-expansion work that we can do by harnessing the reaction in some way at constant pressure and temperature”

$$G = H - TS$$

H = measure of the total energy that can be obtained from the system as heat

TS = measure of the energy that is stored in the random motion of molecules in the system

⇒ Difference (= G) becomes the energy stored in the orderly motion and arrangement of the molecules in the system

Sample problem:

A hard-working human brain, perhaps one that is grappling with physical chemistry, operates at about 25W. What mass of glucose must be consumed to sustain that power output for an hour?