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Course 565/665 Lecture Number _____ Date 4/11/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

SEND AN EMAIL WITH YOUR TOPIC!

Last Time

1st and 2nd Order Phase Transitions

P effects on K_{eq} , ΔG°

$A \xrightleftharpoons{K_{eq}} B$ at constant T

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$-\left(\frac{\partial(\Delta G^\circ/RT)}{\partial p}\right)_T = -\left(\frac{\partial[(G_B^\circ - G_A^\circ)/RT]}{\partial p}\right) = \left(\frac{\partial \ln K_{eq}}{\partial p}\right)$$

We know $G = G(T, p, N)$

$$dG = -SdT + Vdp + \mu dN$$

$$dG = Vdp \quad \text{at constant } T, N$$

$$d\Delta G = \Delta V dp \quad \rightarrow \quad -\left(\frac{\partial(\Delta V dp/RT)}{\partial p}\right) = -\frac{\Delta V}{RT}$$

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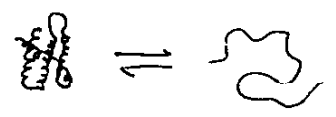
Thus,

$$\left(\frac{\partial \ln K_{eq}}{\partial p} \right)_T = - \frac{\Delta V}{RT}$$

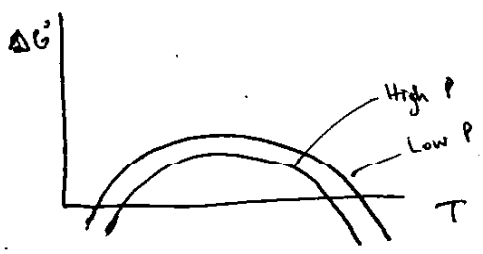
$$\left(\frac{\partial \Delta G^\circ}{\partial p} \right)_T = \Delta V$$

However, there is no established name for this relationship.

Now, let's consider the volume of a protein in solution.



Experiments show that $V_U < V_N$. Proteins have nonpolar groups, and these groups coordinate water in such a way to reduce the volume of the system (protein + water). This is called electrostriction of the protein/water system upon unfolding.



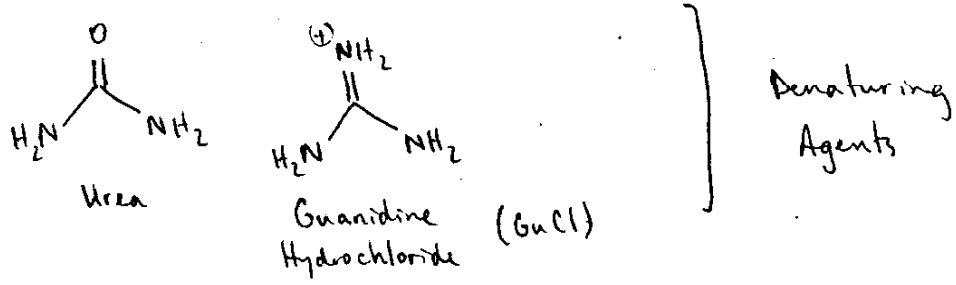
Nonetheless, pressures need to be on the order of 3000 to 10,000 atm to completely unfold proteins. Thus, pressures greater than those found on this planet are needed, so Archea (microorganisms) can live in vents on the bottom of the ocean

and still have stable proteins. Thus, although increased pressures decrease protein stability, the effects are still relatively small.

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Effects of denaturants/denaturing agents on protein stability



Empirically, people have found that

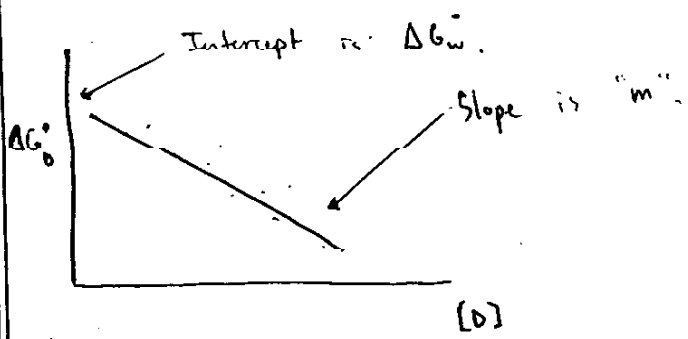
$$\Delta G_D^\circ = \Delta G_W^\circ - m[D]$$

← Concentration of the denaturing agent.

↑
 ΔG° in the presence of denaturants.

↑
 ΔG° in only H_2O .

↑
 Constant specific to a protein with the denaturing agent.



Experimentally

- ① Spectroscopic Probe, [U], [N]
- ② ln K_D
- ③ ΔG_D°
- ④ Repeat 1-3 @ different concentrations of D.

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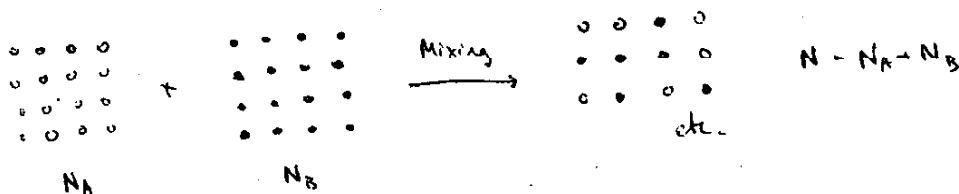
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It is thought that denaturing agents stabilize the unfolded state (lower its energy level relative to the folded state). GuCl is a stronger denaturing agent than Urea.

Chapter 15 - Solutions and Mixtures

- 2 component mixture : $\begin{cases} A \circ \\ B \bullet \end{cases}$

- N site lattice



$$W = \frac{N!}{N_A! N_B!}$$

$$S = k \ln W = k \ln \frac{N!}{N_A! N_B!} = k \ln (N \ln N - N_A \ln N_A - N_B \ln N_B)$$

Before Mixing

(A) $\frac{N_A!}{N_A!} = 1 = W$

Same for
(B)

$S = A S_{mix}$

$S = k \ln W = 0$