"HYDROPHOBIC" "BONDS"

Not a direct electron sharing between hydrophobic molecules - misleading

"Fear of water"
Conveys wrong impression

OIL IN WATER - What happens?

Large oil-water interface

Smaller oil-water interface

OIL droplets combine in order to minimize interfacial surface area.

Why? Because water at the interface has a limited number of ways that it can arrange in order to establish optimal H-bonds with other water.

The oil droplets coalesce not because they "like" each other or because they "hate" water. They do it to maintain as much system entropy as possible, while maintaining approximately the same net H-bonding (enthalpy).
So we say that the hydrophobic effect is entropically driven.

More than 30 years ago, Kauzmann measured $\Delta H$ and $\Delta S$ for the transfer of various molecules from nonpolar solvents to water.

Results: $\Delta H < 0$ Slightly favorable

- The ordered water molecules around the nonpolar solute actually form better H-bonds

$\Delta S < 0$ Very unfavorable. All of those waters are highly ordered.

Similarly

\[
\begin{align*}
\text{Ile} & \text{ Ala} & \text{ Phe} \\
\text{Leu} & \text{ Ala} & \text{ Phe}
\end{align*}
\]

SAME THING

Unfolding transfers interior of protein to water These side chains is a "nonpolar solvent"

Similarly $\Rightarrow$ unfolding proteins has $\Delta S < 0$
Another observation: (OLD)

Protein unfolding also has $\Delta H$ with a strong temperature dependence. What does this tell us about $\Delta C_p$?

Remember that: $\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p (T_2 - T_1)$

The strong $T$-dependence says that $\Delta C_p \neq 0$

Using $\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p (T_2 - T_1)$

and $\Delta S_{T_2} = \Delta S_{T_1} + \Delta C_p \ln \frac{T_2}{T_1}$

THEN: $\Delta G_T = \Delta H_T - T \Delta S_T$

$= \Delta H_{T_1} + \Delta C_p (T - T_1) - T \Delta S_{T_1} - T \Delta C_p \ln \frac{T}{T_1}$

Plotting this expression yields:

![Graph showing the relationship between $\Delta G$ and $T$]
Phenomenon of "cold denaturation" well-known.

Some proteins denature at low temperatures.

(as well as at high T!)

[Diagram showing temperature (T) vs. denaturation (ΔG) curve with key points labeled: folded protein, denatured protein, narrow window, and best denaturation point.]
Carnot Cycle

\[ q = -w = nRT \eta \text{ for } Q = nRT \eta \text{ and } V \text{ is constant} \]

1. \( PV_1 \) at \( T \text{ that} \)

2. \( P_2 V_2 \) at \( T \text{ that} \)

3. \( PV_3 \) at \( T \text{ cold} \)

4. \( P_4 V_4 \) at \( T \text{ cold} \)

Heat in (work on surroundings):
\[ q > 0 \]
\[ w < 0 \]
\[ q = -w = nRT \eta \frac{V_3}{V} \]

Adiabatic reversible compression:
\[ q = 0 \]
\[ w > 0 \]

Heat out:
\[ q < 0 \]
\[ w > 0 \]
\[ q = -w = nRT \eta \frac{V_3}{V} \]

\[ \Delta E = 0 \]

\[ \int_{T_\text{hot}}^{T_\text{cool}} C_v \, dT = -\frac{nRT}{V} \, dV \]

For step 2:
\[ \int_{T_\text{hot}}^{T_\text{cool}} C_v \, dT = -\int_{V_2}^{V_3} \frac{nRT}{V} \, dV \]

\[ \int_{T_\text{hot}}^{T_\text{cool}} C_v \, \frac{dT}{T} = -\int_{V_2}^{V_3} \frac{nR}{V} \, dV \]

Step 2 \( \rightarrow \) 3
\[ C_v \ln \frac{T_\text{cool}}{T_\text{hot}} = -nR \ln \frac{V_3}{V_2} \]

Step 3 \( \rightarrow \) 4
\[ C_v \ln \frac{T_\text{hot}}{T_\text{cool}} = -nR \ln \frac{V_4}{V_3} \]
Total heat absorbed:

\[ q = q_1 + q_2 + q_3 + q_4 \]

\[ = nR\text{Thot} \ln \frac{V_2}{V_1} + 0 + nR\text{Cold} \ln \frac{V_4}{V_3} \]

Total work:

\[ -W = - (w_1 + w_2 + w_3 + w_4) \]

Work done on surroundings:

\[ = nR\text{Thot} \ln \frac{V_2}{V_1} - CV(\text{Thot} - \text{Thot}) \]

\[ + nR\text{Cold} \ln \frac{V_4}{V_3} - CV(\text{Thot} - \text{Teold}) \]

\[ = nR\text{Thot} \ln \frac{V_2}{V_1} + nR\text{Cold} \ln \frac{V_4}{V_3} \]

Leads to \(-W = q\) for complete cycle. Makes sense:

\[ \Delta E_{\text{Tot}} = 0 = W_{\text{Tot}} + Q_{\text{Tot}} \]

\[ \Rightarrow \text{HAVE CONVERTED HEAT TO WORK} \]

Efficiency:

\[ \text{Efficiency} = \frac{\text{Work done}}{\text{Heat in}} = \frac{W_{\text{Tot}}}{q_1} \]

\[ = \frac{Q_{\text{hot}} + Q_{\text{cold}}}{Q_{\text{hot}}} = 1 + \frac{Q_{\text{cold}}}{Q_{\text{hot}}} \]

Book shows:

\[ = \frac{\text{Thot} - \text{Teold}}{\text{Thot}} < 1.0 \]

\[ \uparrow \text{Cannot achieve 100% efficiency} \]
Conclusion: Heat in at top \( \rightarrow \) Leads to \( \Rightarrow \) Net work

\[ \text{Can reverse to make a heat pump} \]
\[ \Rightarrow \text{Work used to transfer heat} \]