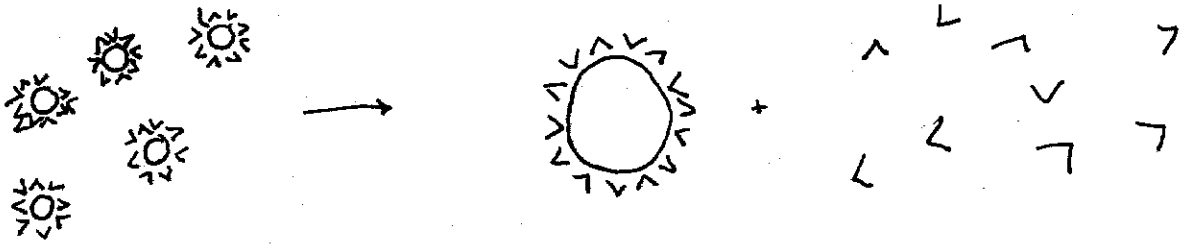
"HYDROPHOBIC" "BONDS"

↙ "Fear of water" Conveys wrong impression

↘ Not a direct electron sharing between hydrophobic molecules – misleading

This is to contrary in ΔS_{mixing}, in general. WHY?

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).

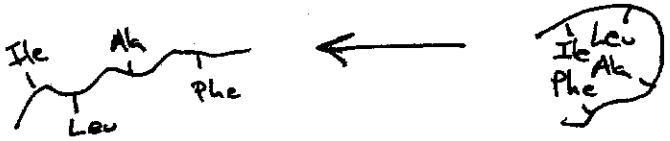
So we say that the hydrophobic effect is entropically driven

More than 30 years ago, Kauzmann measured ΔH and ΔS 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



SAME THING

unfolding transfers these side chains to water

interior of protein is a "nonpolar solvent"

Similar → unfolding proteins has $\Delta S < 0$

Another observation: (OLD)

Model studies

ΔH shows a strong temperature dependence

Protein unfolding also has ΔH with a strong temperature dependence. What does this tell us about ΔC_p?

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

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

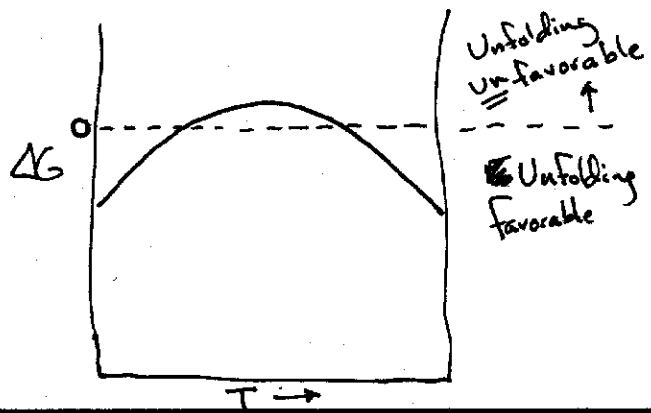
Using $\Delta H_{T_\bullet} = \Delta H_{T_h} + \Delta C_p (T_\bullet - T_h)$ T_h and T_s reference temps

and $\Delta S_{T_\bullet} = \Delta S_{T_s} + \Delta C_p \ln T_\bullet / T_s$

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

$= \Delta H_{T_h} + \Delta C_p (T - T_h) - T\Delta S_{T_s} - T\Delta C_p \ln T/T_s$

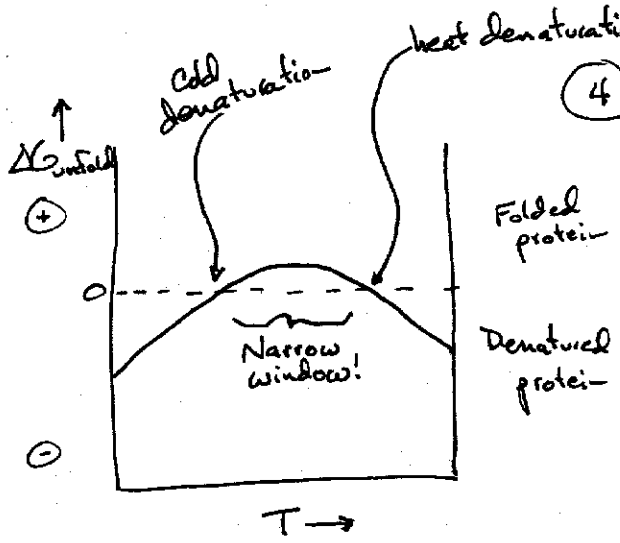
Plotting this expression yields:



Phenomenon of
"cold denaturation"
well-known.

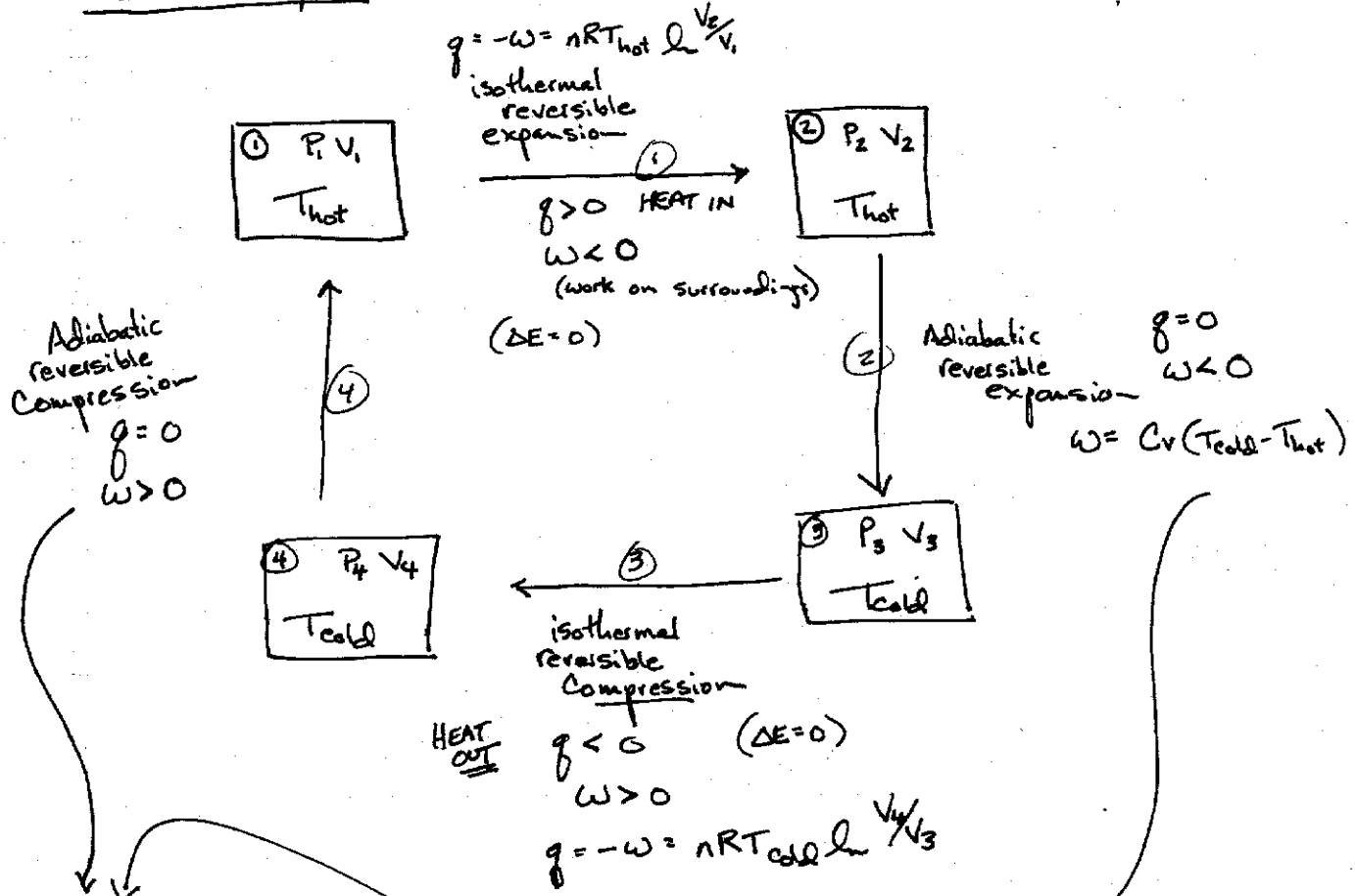
Some proteins denature
at <u>low temperatures</u>.

(as well as at high T!)



Carnot Cycle

→ Gas in a piston



$$dw = C_v\,dT$$

but also $dw = -P\,dV$ $\Rightarrow \therefore \quad C_v\,dT = -\frac{nRT}{V}\,dV$

For step 2:

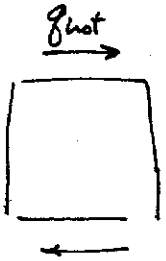
$$\int_{T_{hot}}^{T_{cold}} C_v\,dT = -\int_{V_2}^{V_3} nRT\,\frac{dV}{V}$$

Divide by T

$$\int_{T_{hot}}^{T_{cold}} C_v\,\frac{dT}{T} = -\int_{V_2}^{V_3} nR\,\frac{dV}{V}$$

Step ②→③ $\quad C_v \ln \frac{T_{cold}}{T_{hot}} = -nR \ln V_3/V_2$

Step ④→① $\quad C_v \ln \frac{T_{hot}}{T_{cold}} = -nR \ln V_1/V_4$



Total heat absorbed:

$$q = q_1 + q_2 + q_3 + q_4$$

$$= nRT_{hot} \ln V_2/V_1 + 0 + nRT_{cold} \ln V_4/V_3$$

Total work:

$$-w = -(w_1 + w_2 + w_3 + w_4)$$

Work done on surroundings

$$= nRT_{hot} \ln V_2/V_1 - C_V(T_{cold} - T_{hot})$$

$$+ nRT_{cold} \ln V_4/V_3 - C_V(T_{hot} - T_{cold})$$

$$= nRT_{hot} \ln V_2/V_1 + nRT_{cold} \ln V_4/V_3$$

Leads to $-w = q$ for complete cycle. Makes sense

$$\Delta E_{TOT} = 0 = w_{TOT} + q_{TOT}$$

$\Rightarrow$ HAVE CONVERTED HEAT TO WORK

$$\text{Efficiency} = \frac{\text{Work out}}{\text{Heat in}} = \frac{\text{Work done}}{\text{Heat in}} = \frac{w_{TOT}}{q_1}$$

$$= \frac{q_{hot} + q_{COLD}}{q_{hot}} = 1 + \frac{q_{cold}}{q_{hot}}$$

Book shows:

$$= \frac{T_{hot} - T_{cold}}{T_{hot}} < 1.0$$

↑ Cannot achieve 100% efficiency

Conclusion: Heat in at top (Throw off heat out at bottom)

↙ Leads to

Net work

Can reverse to make a heat pump

↳ Work used to transfer heat