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FACULTY OF NATURAL SCIENCE
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The theme:

Chemical potential. Chemical potential of an ideal gas

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FREE ENERGY AND EQUILIBRIA

$\Delta G < 0$ process is spontaneous

$\Delta G > 0$ *reverse* process is spontaneous

$\Delta G = 0$ no change is spontaneous: **Equilibrium**

Le Châtelier's principle gives us some understanding of how the equilibrium of a system changes when we perturb it.

"Any change in one of the variables that determines the state of a system in equilibrium causes a shift in the position of equilibrium in a direction that tends to counteract the change in the variable under consideration."

We are interested in how systems tend towards equilibrium and what obstacles keep them out of equilibrium.

The free energy, or more correctly, the ***chemical potential*** is our measure of roughly how far we have to go to come to equilibrium. It is a potential energy of sorts.

CHEMICAL POTENTIAL

The chemical potential can be used to give quantitative meaning to Le Châtelier's principle.

Chemical potential of component A, μ_A, is defined as the partial molar Gibbs free energy:

$$\mu_A \equiv \left(\frac{\partial G}{\partial n_A} \right)_{T, P, n_j \neq n_A}$$

This is the change in G with respect to a infinitesimal change in the amount of component A with all other parameters held constant.

It is essentially the free energy increase (or decrease) associated with adding a little of A to the system.

DIRECTIONALITY OF A CHEMICAL REACTION

Consider a closed system of four components (A, B, C, and D) undergoing a reversible chemical reaction:

$$aA + bB \leftrightarrow cC + dD$$

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

In a closed system,

$$\frac{dn_A}{a} = \frac{dn_B}{b} = -\frac{dn_c}{c} = -\frac{dn_d}{d} \equiv -d\alpha$$

$$dn_A = -a\,d\alpha$$

$$dn_B = -b\,d\alpha$$

M

At constant T and P,

$$dG = \sum_i \mu_i dn_i$$

$$= (c\mu_C + d\mu_D - a\mu_A - b\mu_B)d\alpha$$

$$= -\left((a\mu_A + b\mu_B) - (c\mu_C + d\mu_D)\right)d\alpha$$

At equilibrium:

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D$$

EXAMPLE

$$H_2O\,(l) \underset{}{\overset{100\ ^\circ C}{\rightleftharpoons}} H_2O\,(g)$$

This is at **constant T and P**. Its **reversible**. So,

$$\Delta G^\circ_{vap} = 0 = \Delta H^\circ_{vap} - T\,\Delta S^\circ_{vap}$$

Note that this implies **at equilibrium**:

$$\mu_{H_2O(l)} = \mu_{H_2O(g)}$$

CHEMICAL POTENTIAL AND PARTIAL PRESSURE

We found last time that $G(P_2) - G(P_1) = nRT \ln\left(\frac{P_2}{P_1}\right)$ (T = constant)

Defining the standard state: $G(P_1 = 1atm) \equiv G^0$

Then,

$$G(P) = G^0 + nRT \ln\left(\frac{P}{1atm}\right)$$

and,

$$\mu_A \equiv \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_j \neq n_A}$$

so,

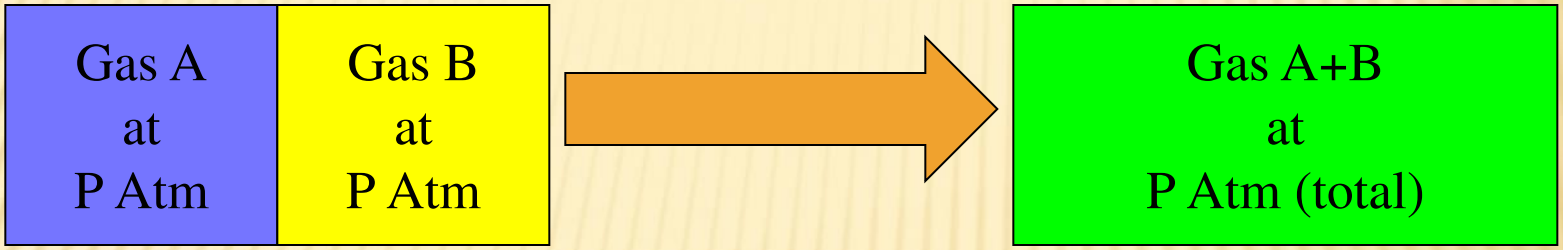
$$\mu = \mu^0 + RT \ln\left(\frac{P}{1atm}\right)$$

In a mixture, the chemical potential of A can thus be expressed in terms of its partial pressure and its standard (pure) chemical potential:

$$\mu_A = \mu_A^0 + RT \ln\left(\frac{P_A}{1atm}\right)$$

ΔG OF MIXING

Consider the isobaric, isothermal mixing of two gases:



$$\Delta G_{mix} = n_A RT \ln X_A + n_B RT \ln X_B$$

$$\Delta G_{mix} = -T\Delta S_{mix}$$

$$\Delta S_{mix} = -n_A R \ln X_A - n_B R \ln X_B$$

$$X_i \equiv \frac{n_i}{\sum_j n_j}$$ Mole Fraction component i

$$X_A = \frac{n_A}{n_A + n_B} \text{ and } X_B = \frac{n_B}{n_A + n_B}$$

EQUILIBRIUM CONSTANT

The Haber process of nitrogen fixation: $N_2 + 3H_2 \rightarrow 2NH_3$

$$\Delta G = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

$$= 2\left(\mu^0_{NH_3} + RT\ln\left(\frac{P_{NH_3}}{1atm}\right)\right) - \left(\mu^0_{N_2} + RT\ln\left(\frac{P_{N_2}}{1atm}\right)\right) - 3\left(\mu^0_{H_2} + RT\ln\left(\frac{P_{H_2}}{1atm}\right)\right)$$

Rewrite letting $P_i = \frac{P_i}{1atm}$ ~~un~~itless pressure ratio. No units inside "ln".

$$\Delta G = \boxed{2\mu^0_{NH_3} - \mu^0_{N_2} - 3\mu^0_{H_2}} + RT\left(2\ln P_{NH_3} - \ln P_{N_2} - 3\ln P_{H_2}\right)$$

$$= \boxed{\Delta G^0} + RT\left(\ln\left(\frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}\right)\right)$$

We have used the identity: $a\ln x = \ln x^a$

EQUILIBRIUM CONSTANT

At any temperature and pressure there exists and equilibrium state for this reaction.

A combination of $P_{N_2}, P_{H_2}, P_{NH_3}$ such that $\Delta G = 0$.

$$\Delta G = \Delta G^0 + RT\left(\ln\left(\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}\right)\right)$$

$$0 = \Delta G^0 + RT\left(\ln\left(\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}\right)\right)$$

$$\Delta G^0 = -RT\left(\ln\left(\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}\right)\right)$$

This equation holds for equilibrium values of $P_{N_2}, P_{H_2}, P_{NH_3}$

EQUILIBRIUM CONSTANT

$$\Delta G^0 = -RT\left(\ln\left(\frac{\left(P_{NH_3}^{eq}\right)^2}{\left(P_{N_2}^{eq}\right)\left(P_{H_2}^{eq}\right)^3}\right)\right)$$

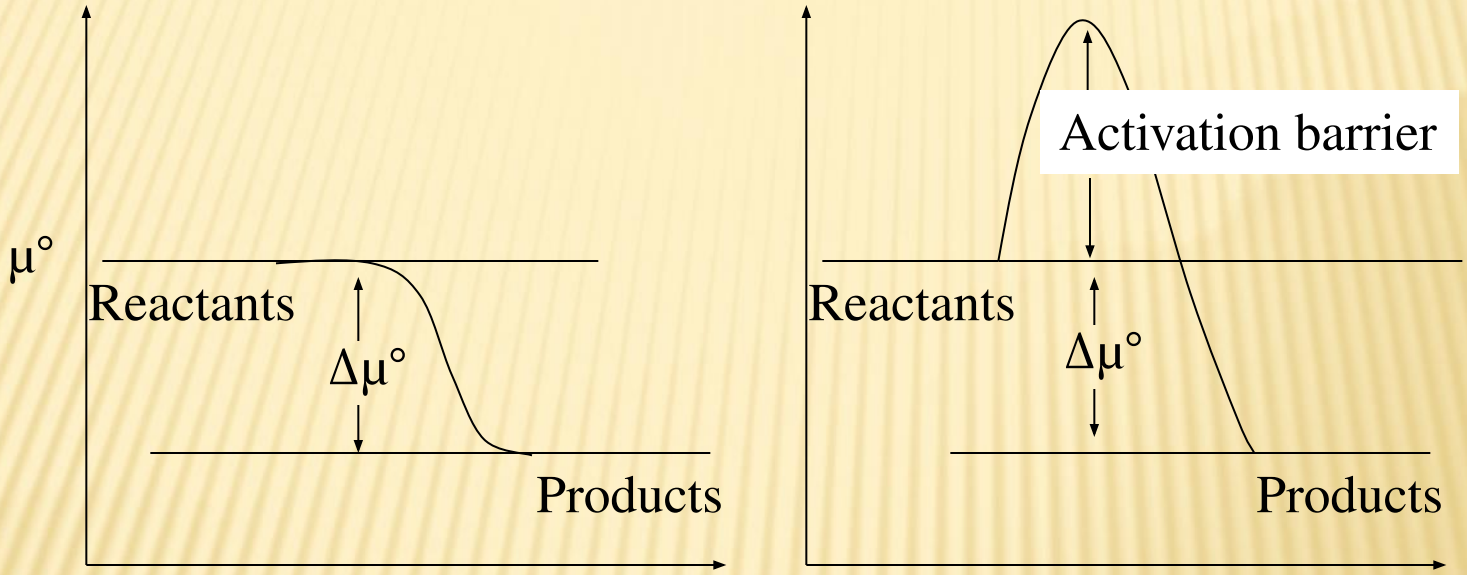
Define equilibrium constant (at constant T and P):

$$K = \frac{\left(P_{NH_3}^{eq}\right)^2}{\left(P_{N_2}^{eq}\right)\left(P_{H_2}^{eq}\right)^3} \qquad \Delta G^0 = -RT\ln K$$

More generally: $aA + bB \longrightarrow cC + dD$ $\qquad K = \frac{\left(P_C^{eq}\right)^c\left(P_D^{eq}\right)^d}{\left(P_A^{eq}\right)^a\left(P_B^{eq}\right)^b}$

Most generally: $K \equiv \frac{\prod_{products}\left(P_i^{eq}\right)^{n_i}}{\prod_{reactants}\left(P_i^{eq}\right)^{n_i}}$ $\qquad Q \equiv \frac{\prod_{products}\left(P_i\right)^{n_i}}{\prod_{reactants}\left(P_i\right)^{n_i}}$

CHEMICAL POTENTIAL EXAMPLE



Chemical potential is a measure of the *thermodynamic free energy*.
It tells us what the *equilibrium distribution* of reactants and products must be
It does **not** tell us the *kinetic rate*.

EQUILIBRIUM EXAMPLE

Oxidation of CO: $2\ CO\ (g) + O_2\ (g) \rightarrow 2\ CO_2\ (g)$

The free energy change for this reaction is simply:

$$\Delta G^\circ_{rxn} = 2\ \Delta G^\circ_{289}(CO_2) - 2\ \Delta G^\circ_{289}(CO) - \Delta G^\circ_{289}(O_2)$$

We can calculate this using numbers from the appendix:

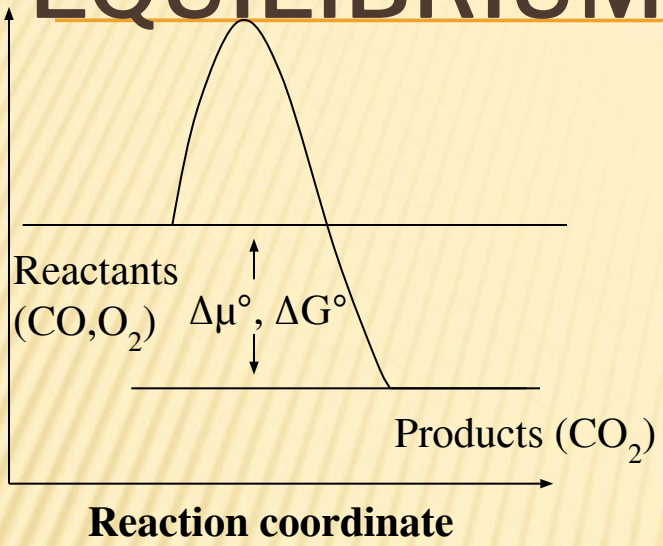
$$\Delta G^\circ_{rxn} = 2\ (-394.36) - 2(\ -137.17) - 0\ \ (kJ/mol) = -514.38\ kJ/mol$$

A relatively large negative number.

$$\Delta G^\circ_{rxn} = -RT\ln K \qquad K = e^{514{,}380/RT} = e^{207} = \frac{\left(P^{eq}_{CO_2}\right)^2}{\left(P^{eq}_{O_2}\right)\left(P^{eq}_{CO}\right)^2}$$

The equilibrium for this reaction lies far in favor of the products.
Large negative ΔG means the reaction goes forward with high probability.

EQUILIBRIUM EXAMPLE



The conversion of CO and O_2 to CO_2 is energetically favorable, but the reaction is slow

1) We have to first break an O-O double bond
2) The resultant atoms of oxygen must then react with CO.

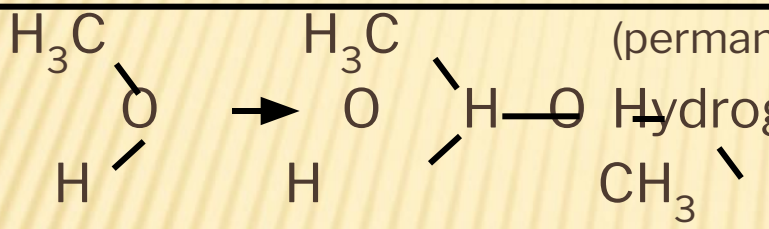
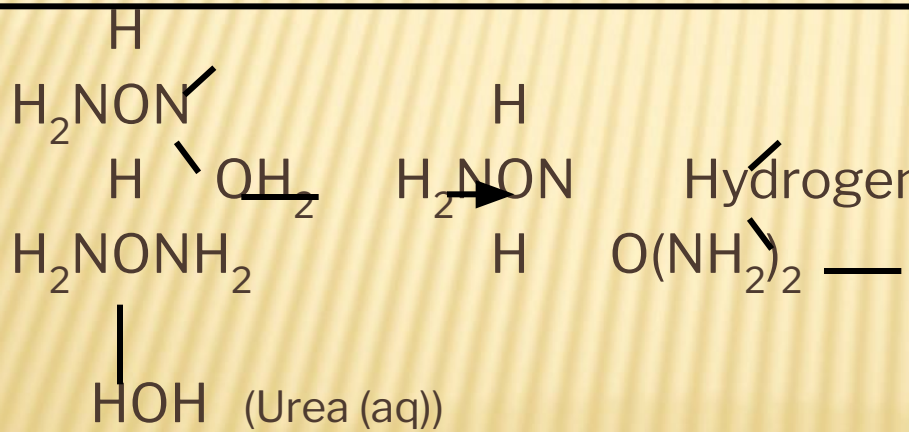
For other reactions like

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

We need a catalyst (e.g. platinum surface), and ideally we wish to convert the released energy to work.

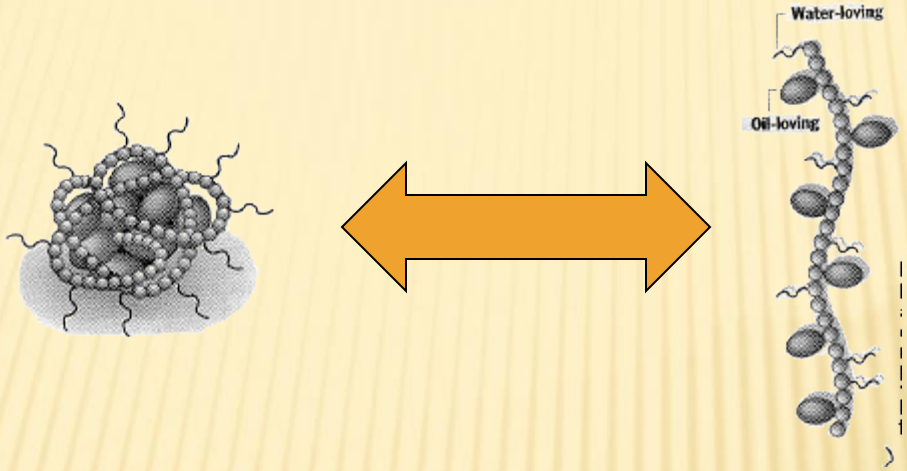
Catalysts enable a reaction to take an alternative path, with lower activation barrier.

ΔH^0 FOR SOME NONCOVALENT INTERACTIONS

Reaction	Interaction	ΔH^0(kJ mol^{-1})
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	Ionic	-785
$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$	Ionic +ion-dipole	+4
$Ar(g) \rightarrow Ar(s)$	London (fluctuation dipole)	-8
$Acetone(g) \rightarrow Acetone(l)$	London-van der Waals	-30
	(permanent dipole) Hydrogen bond	-20
 (Urea (aq))	Hydrogen bond (aq)	-5
$C_3H_6(l) + H_2O(l) \rightarrow C_3H_6(aq)$	Hydrophobic	-10

(TSWP p. 98)

PROTEIN UNFOLDING



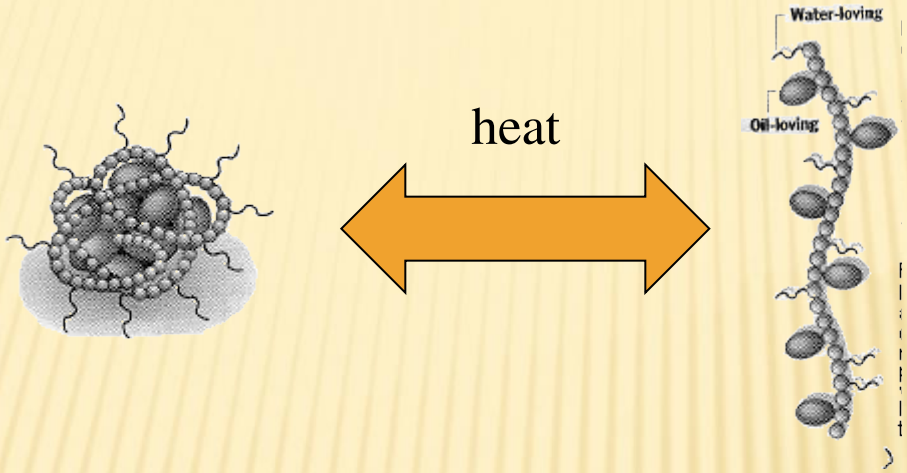
Proteins have a native state. (Really, they tend to have a tight cluster of native states.)

Denaturation occurs when heat or denaturants such as guanidine, urea or detergent are added to solution. Also, the pH can affect folding.

When performing a denaturation process non-covalent interactions are broken.

Ionic, van der-Waals, dipolar, hydrogen bonding, etc.
Solvent is reorganized.

PROTEIN UNFOLDING

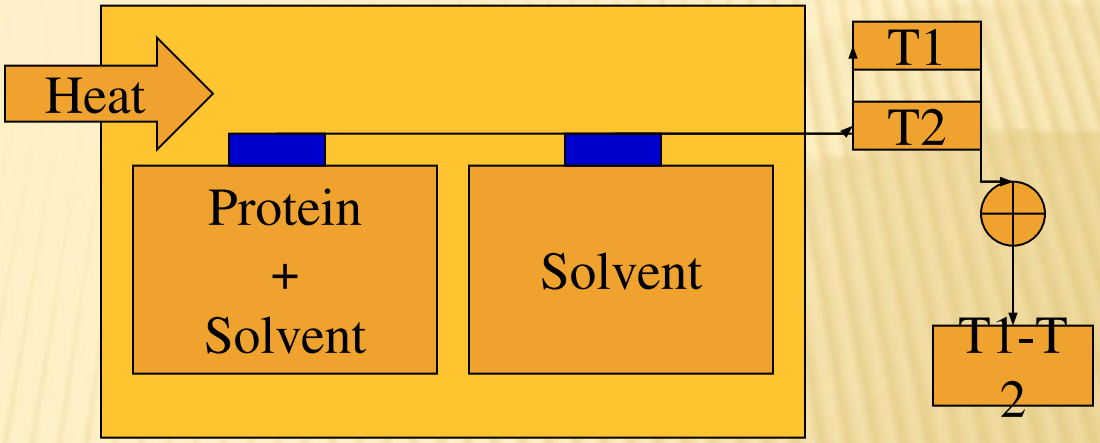


Let's consider denaturation with heat. We can determine a great deal about the nature of the protein from such a consideration.

The experimental technique we use for measuring thermodynamic changes here is the differential scanning calorimeter.

Basic experiment: Add heat to sample, measure its temperature change.

PROTEIN UNFOLDING



In differential scanning calorimetry you have two samples:

Your material of interest

Control

You put in an amount of heat to raise the temperature of the control at a constant rate, then measure the rate of change in temperature of the other sample as a function of the input heat.

This is a measure of the heat capacity!

PROTEIN UNFOLDING

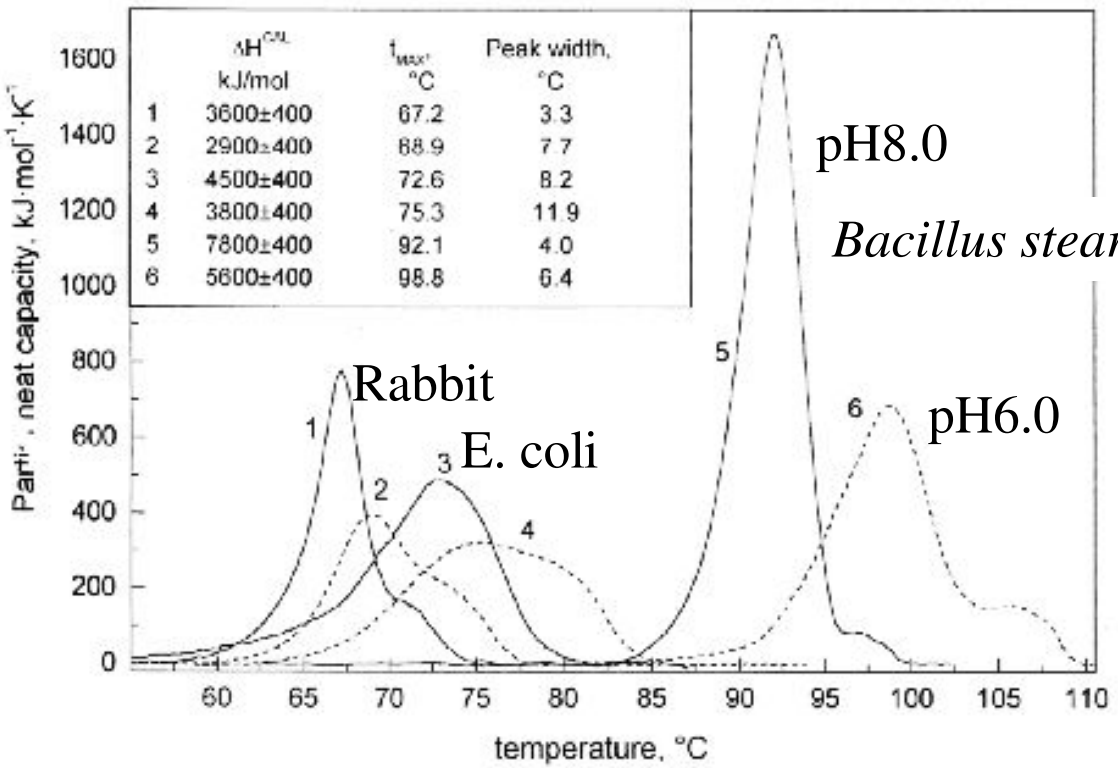


Fig. 1. Differential scanning thermograms of GAPDHs isolated from rabbit muscle (1,2), *E. coli* (3,4) and *B. stearothermophilus* (5,6). Holoenzymes were used, the protein concentrations being 1 mg/ml (7.1 μM calculated per tetramer). The measurements were performed in 100 mM KH_2PO_4–KOH buffer containing 1 mM NAD^+ at pH 8.0 (samples 1, 3 and 5) and pH 6.0 (samples 2, 4 and 6). Heating rate, 1°C/min. The widths of the peaks were measured at half-heights of the peaks.

Data for glyceraldehyde-3-phosphate dehydrogenase.

Is the protein more stable at pH 8 or 6? Why is B. stear. more stable?

PROTEIN UNFOLDING

We are given the following data for the denaturation of lysozyme:

	10	25	60	100 °C
ΔG° kJ/mol	67.4	60.7	27.8	-41.4
ΔH° kJ/mol	137	236	469	732
ΔS° J/ K mol	297	586	1318	2067
$T\Delta S^\circ$ kJ/mol	69.9	175	439	771

Where is the denaturation temperature?

What then is special about the temperature at which the denaturation is spontaneous?