Física do Corpo Humano

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Segunda Lei da Termodinâmica
Aplicações em Biologia

B05

Entalpia, *H* (B03)

Função de estado chamado de entalpia:

$$H = U + pV$$

Apesar de w depender do caminho $w = -p_{\text{ext}}\Delta V$

U, *p* e *V* separadamente são funções de estado

- Quando a entalpia varia muito lentamente

$$\begin{aligned}\Delta H &= \Delta(U + pV) \\ &= \Delta U + \Delta(pV) \\ &= \Delta U + p\Delta V + V\Delta p\end{aligned}$$

Entalpia, *H* (B03)

Se p é constante

$$\begin{aligned}\Delta H &= \Delta U + p\Delta V + V(\Delta p = 0)\\ &= (\Delta U = Q + w) + p\Delta V\\ &= Q|_p + (w = -p\Delta V) + p\Delta V\end{aligned}$$

$$\boxed{\Delta H = Q|_p}$$

H é um componente da função de estado energia livre de Gibbs, *G*, no qual se prevê a direção de alteração espontânea por um processo a pressão e temperatura constante - as restrições experimentais preferidas do cientista biológica.

Ciclo de Carnot (B04)

Para um processo reversível

$$\oint \frac{\delta Q}{T} = 0$$

Ou seja, a integral abaixo é independente de caminho

$$\int_L \frac{\delta Q}{T}$$

$$\boxed{dS = \frac{\delta Q}{T}}$$

S é uma função de estado chamado de Entropia

Entropia é um índice da tendência de um sistema fazer uma mudança expontânea

Transformação Reversível

Suponha que uma célula realize uma transformação reversível a pressão constante e libere um calor q para o ambiente em torno

$$\boxed{\Delta S_{\text{vizinhanca}} = -\frac{Q|_p}{T}}$$

Como as temperaturas são praticamente as mesmas (célula e vizinhança)

$$\Delta T \approx 0$$

O trabalho pV é praticamente desprezível e

$$Q|_p = \Delta H \quad \longrightarrow \quad \Delta S_{\text{vizinhanca}} = -\frac{\Delta H}{T}$$

Desnaturação de proteínas

$$\Delta S_{\text{vizinhanca}} = -\frac{\Delta H}{T}$$

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p}$$

$$\Delta S_{\text{d}} = \frac{\Delta H_d}{T_m}$$

$$\Delta S_{\text{d}} = C_p \frac{\Delta T}{T_m}$$

$$dS_{\text{d}} = C_p \frac{dT}{T_m}$$

$$\Delta S\Big|_{T_1}^{T_2} = \int_{T_1}^{T_2} C_p \frac{dT}{T_m}$$

$$= C_p \ln\left(\frac{T_2}{T_1}\right)$$

Desnaturação de proteínas

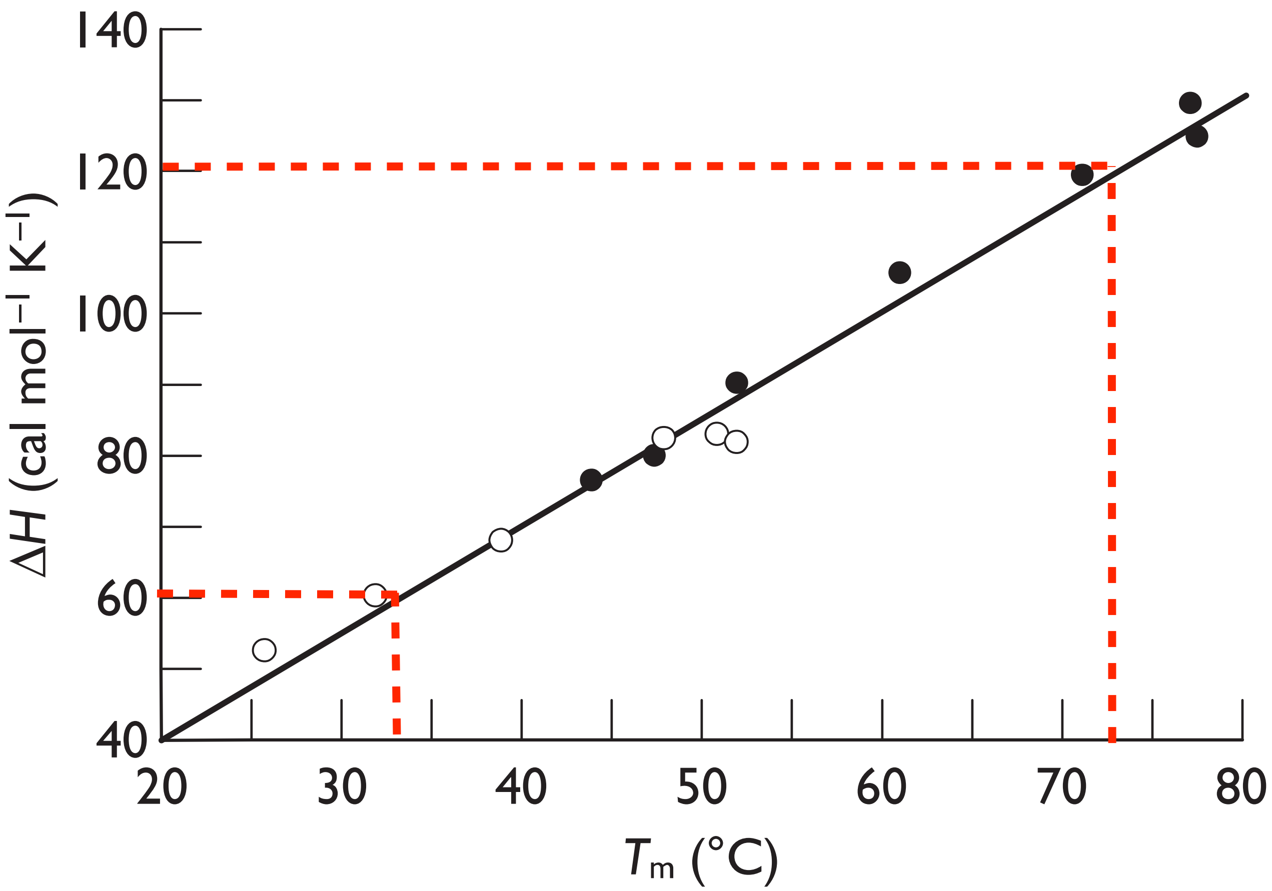
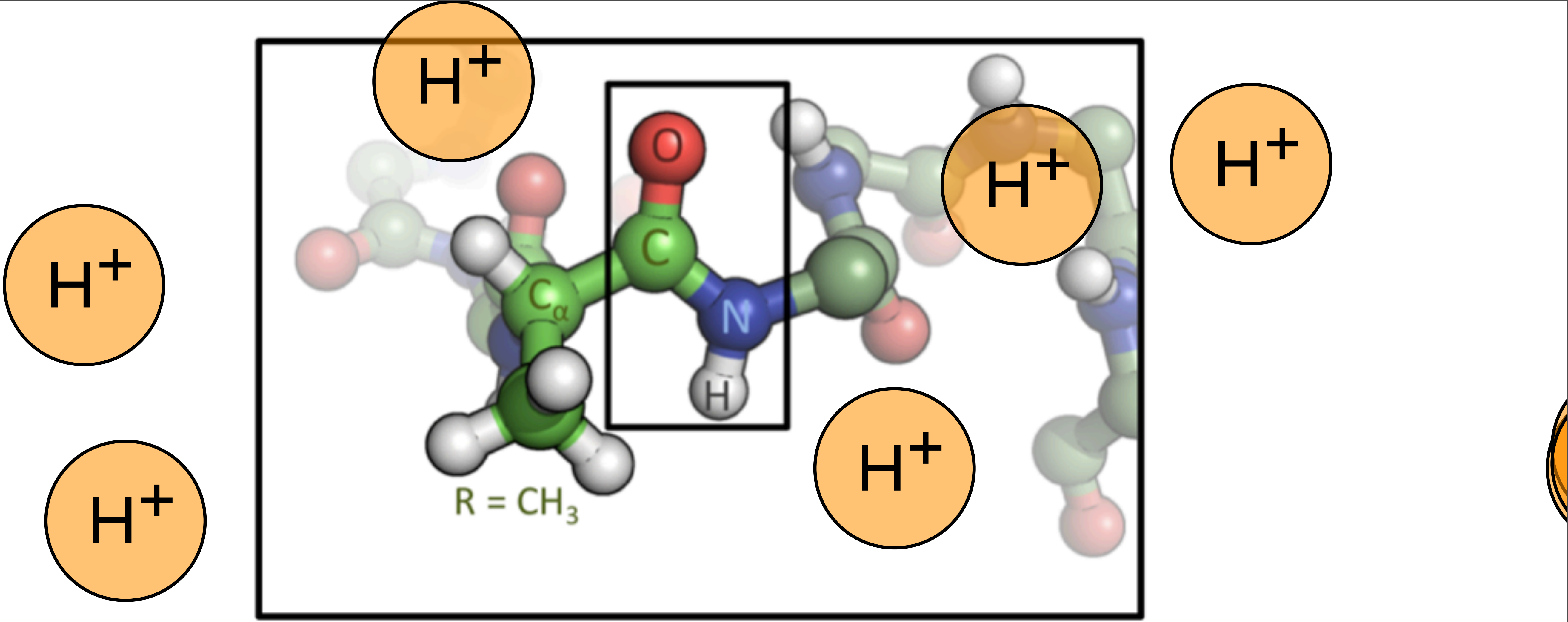
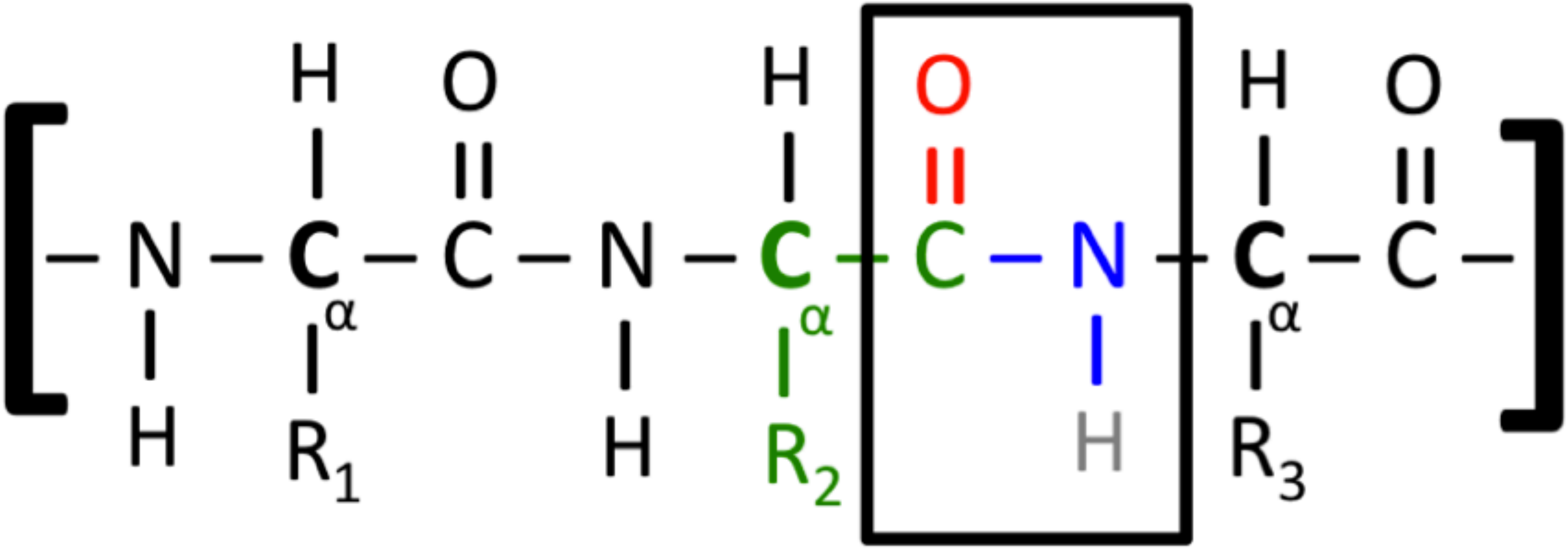


Fig. 2.7 Enthalpy of unfolding of hen egg white lysozyme as a function of transition temperature. Filled symbols: intact lysozyme. Open symbols: lysozyme in which one of the four native disulfide bonds has been removed. When folded, 3-SS lysozyme closely resembles the native state of intact lysozyme. Change in transition temperature was induced by a change of pH. Note that ΔH is approximately linear in T_m. The data are from Cooper *et al.* (1991).

$$\Delta S_d = \frac{\Delta H_d}{T_m}$$





$$\left[-\underset{\mathrm{H}}{\mathrm{N}}-\underset{\mathrm{R_1}}{\overset{\mathrm{H}}{\mathrm{C}^{\alpha}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{N}}-\underset{\mathrm{R_2}}{\overset{\mathrm{H}}{\mathrm{C}^{\alpha}}}-\boxed{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{N}}}-\underset{\mathrm{R_3}}{\overset{\mathrm{H}}{\mathrm{C}^{\alpha}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right]$$

Terceira Lei da Termodinâmica

A entropia de um cristal perfeito a temperatura absoluta igual a zero é igual a zero.

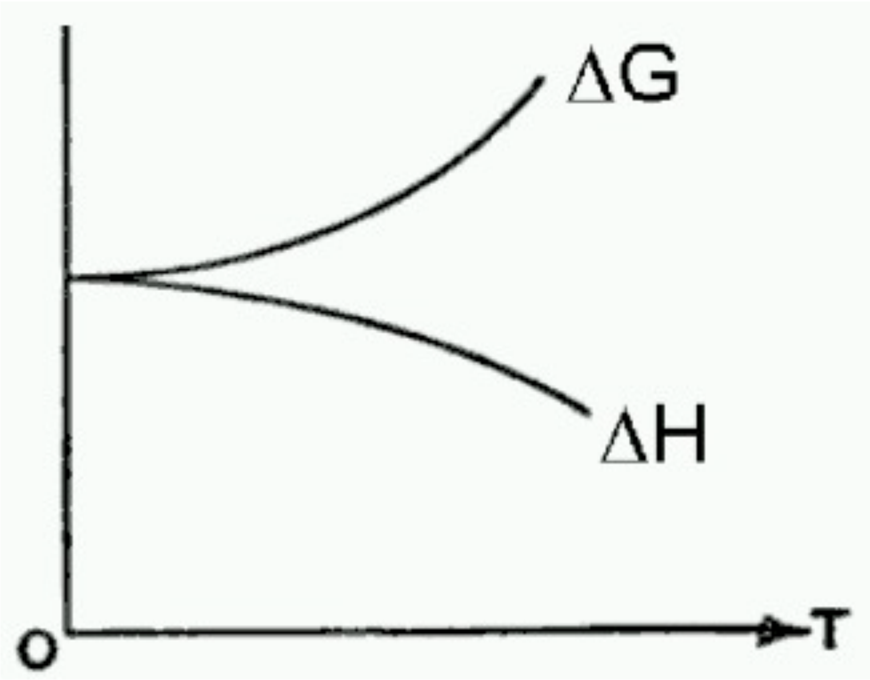
Sendo isso verdade, um cristal perfeito só possui um estado Ω com mínimo de energia

$$S = k_B \ln(\Omega)$$

Teorema de Nernst $\lim_{T \to 0} \Delta S = 0$

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$



Equilíbrio

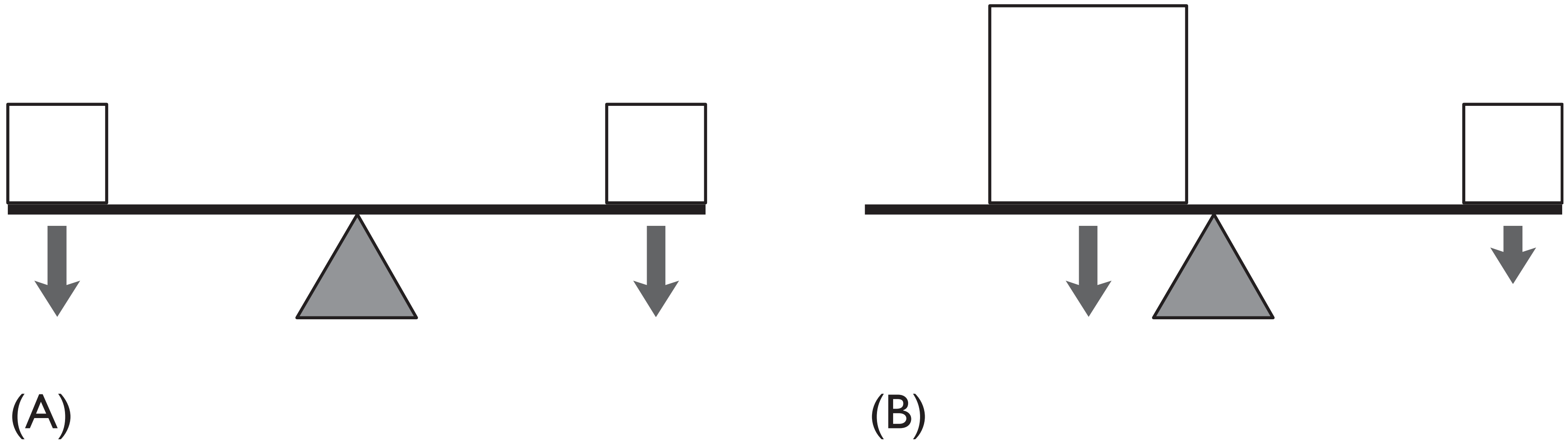


Fig. 4.2 Equilibrium. We know from experience that if the weights are the same, as in panel (A), the distance of each weight from the fulcrum must be the same. But if the weights are different, as in panel (B), the distance from the fulcrum cannot be the same. The lighter weight must be farther from the fulcrum than the heavier weight. By Newton's Second Law, at equilibrium the clockwise torque equals the counterclockwise torque, where torque = mass × gravitational acceleration × distance from fulcrum.

Equilíbrio

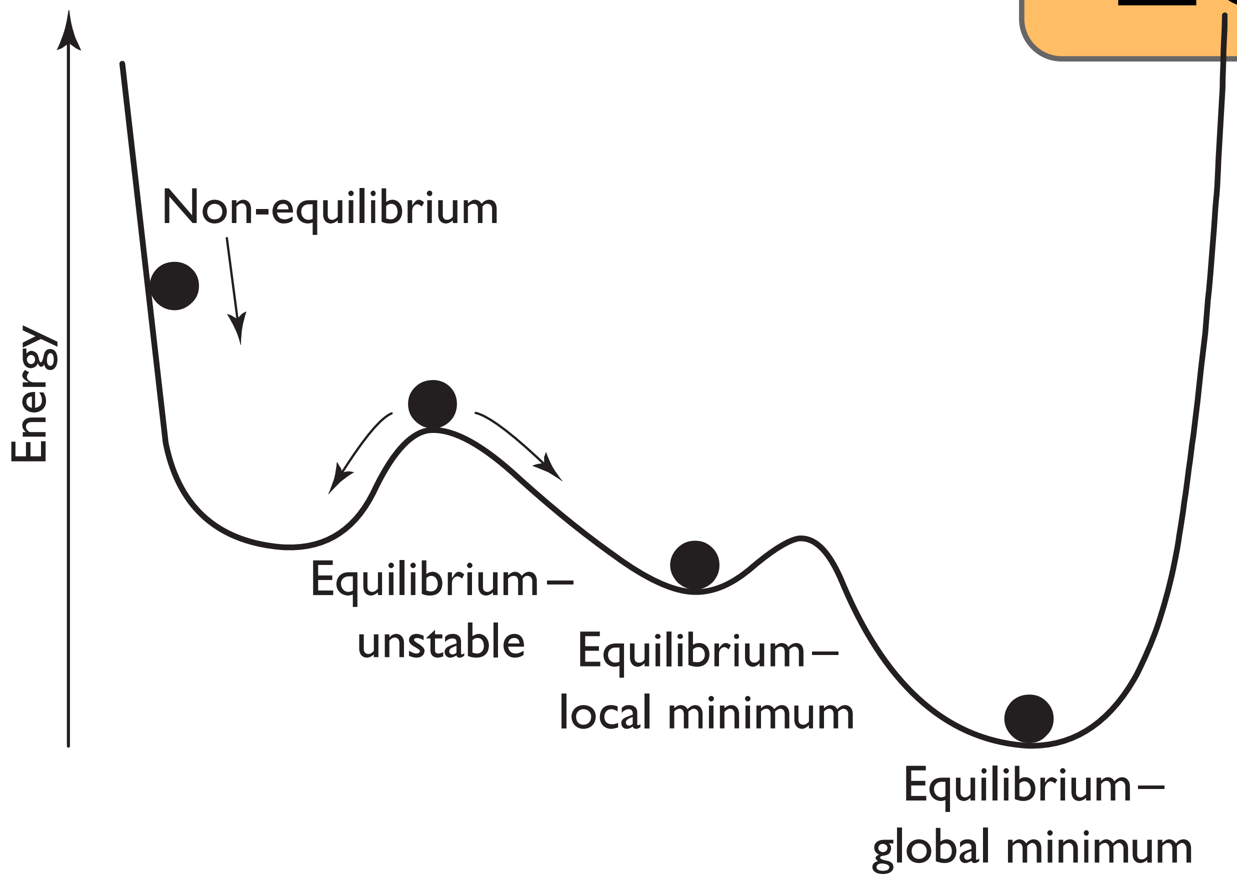
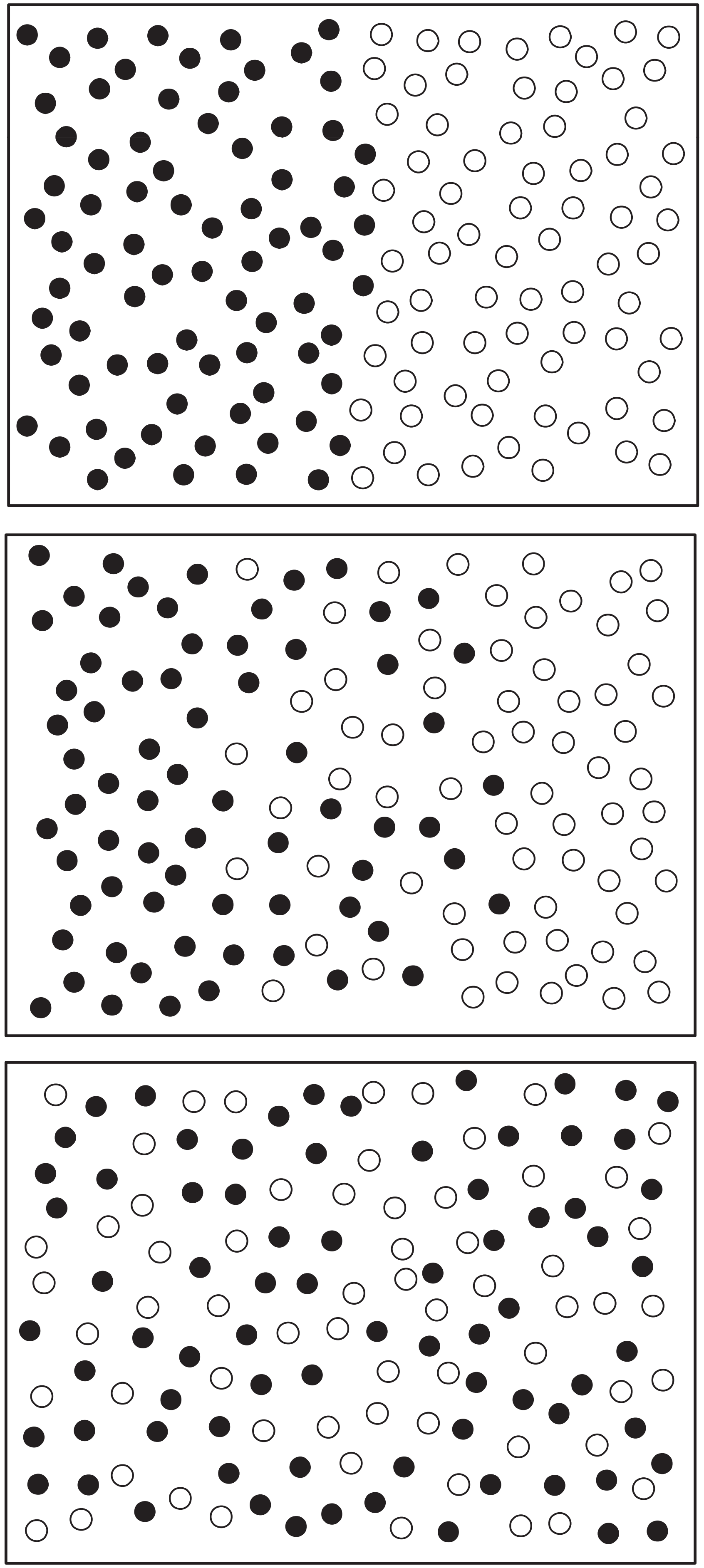


Fig. 4.3 Different types of equilibrium. The non-equilibrium situation will change immediately. The unstable equilibrium, like the snow at rest on a mountainside, will not change without the addition of energy. But the amount of energy needed to get over the barrier is very small. There are two main types of energy minimum: local minimum and global minimum. A local minimum has the lowest energy in the vicinity. The global minimum has the lowest free energy of all. An ongoing debate in protein folding research is whether the folded state of a protein corresponds to a local or a global free energy minimum. In some case, the functional state of a protein or enzyme might be a kinetically trapped conformation.

Equilíbrio



Maxiumum free energy
Minimum entropy

$t = 0$

$t > 0$

Minimum free energy
Maximum entropy

$t \to \infty$

Fig. 4.4 Mixing. At time $t = 0$, when the partition is removed, the liquids are completely separate. The liquids are miscible so mixing occurs. After a sufficiently long time, the liquids are completely mixed. The unmixed state has a maximum of free energy for the system and a minimum of entropy. The completely mixed state has a minimum of free energy and a maximum of entropy. Based on Fig. 1.5 of van Holde (1985).

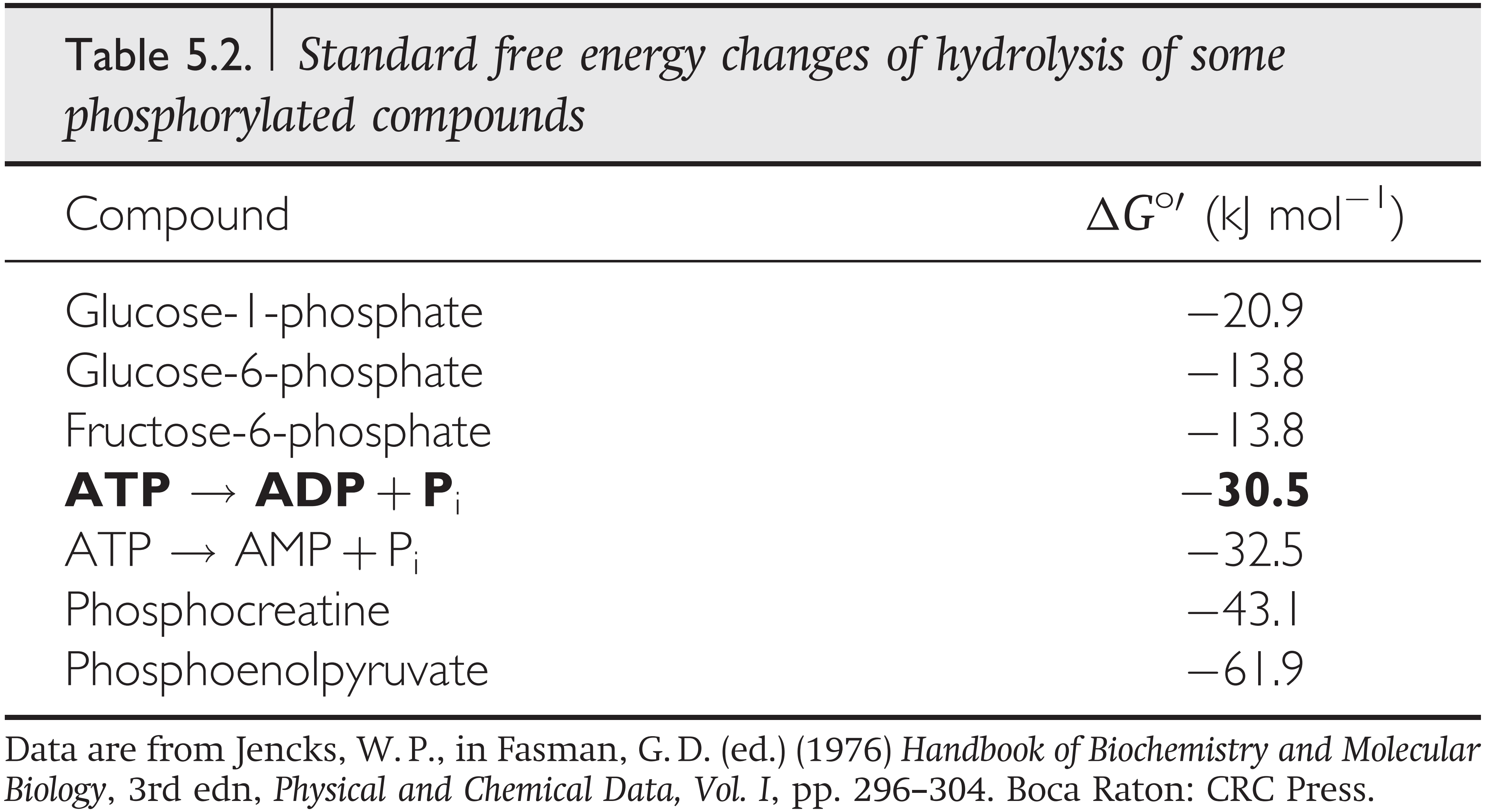


Table 5.2. *Standard free energy changes of hydrolysis of some phosphorylated compounds*

Compound	$\Delta G^{\circ\prime}$ (kJ mol^{-1})
Glucose-1-phosphate	−20.9
Glucose-6-phosphate	−13.8
Fructose-6-phosphate	−13.8
$\mathbf{ATP} \rightarrow \mathbf{ADP} + \mathbf{P}_i$	**−30.5**
$ATP \rightarrow AMP + P_i$	−32.5
Phosphocreatine	−43.1
Phosphoenolpyruvate	−61.9

Data are from Jencks, W. P., in Fasman, G. D. (ed.) (1976) *Handbook of Biochemistry and Molecular Biology*, 3rd edn, *Physical and Chemical Data, Vol. I*, pp. 296–304. Boca Raton: CRC Press.

Osmose

Equação fundamental da Termodinâmica Química, para um sistema contendo n espécies, com a i-ezima espécie contendo Ni partículas

$$dG = -SdT + Vdp + \sum_{i}^{n} \mu_i dN_i$$

se T e p são constantes:

$$\sum_{i}^{n} \mu_i dN_i = \mu_1 dN_1 + \mu_2 dN_2 + \ldots$$

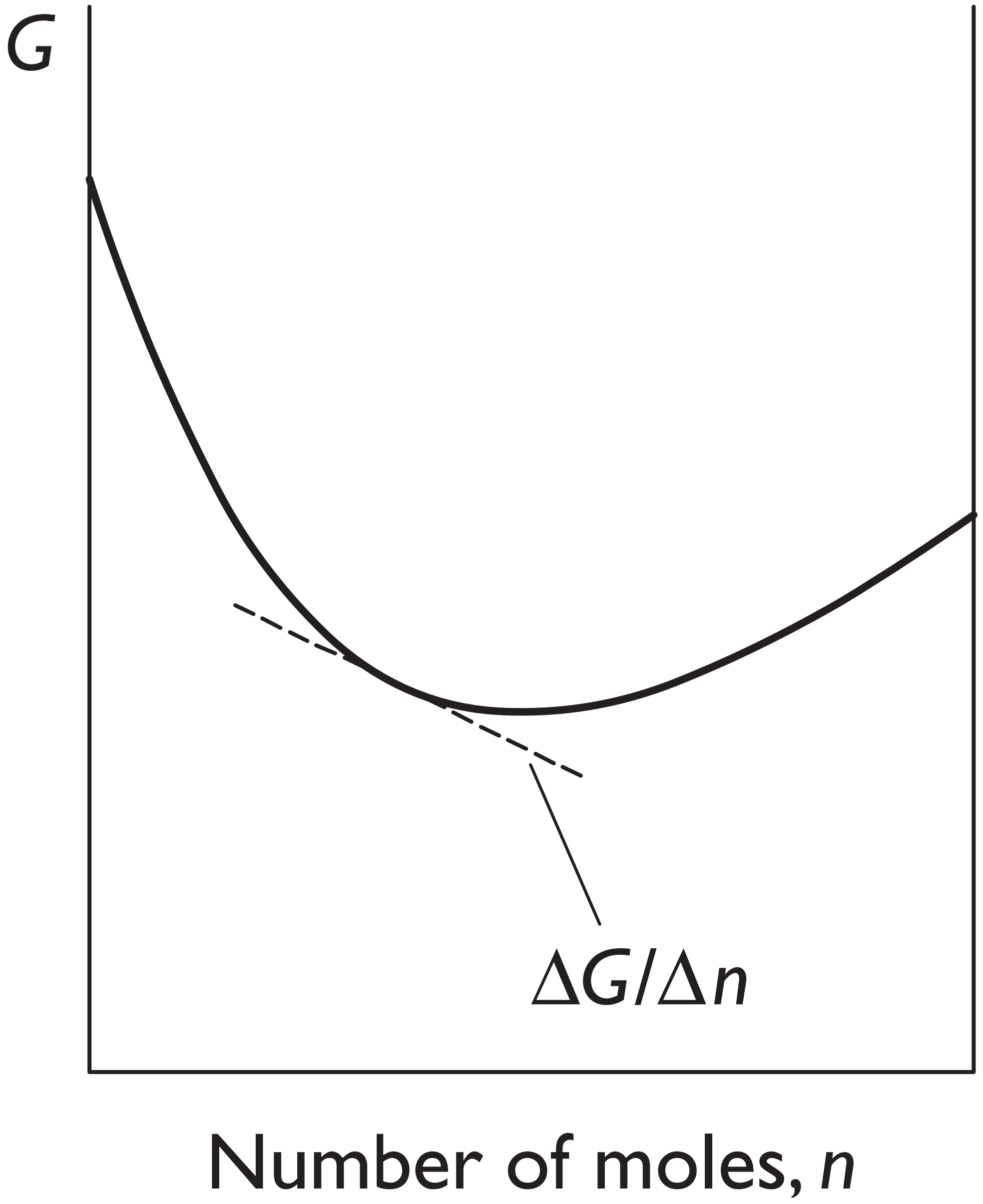
Inclinação da energia livre com relação ao numero de partículas

A definição de potencial químico do elemento i

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}}$$

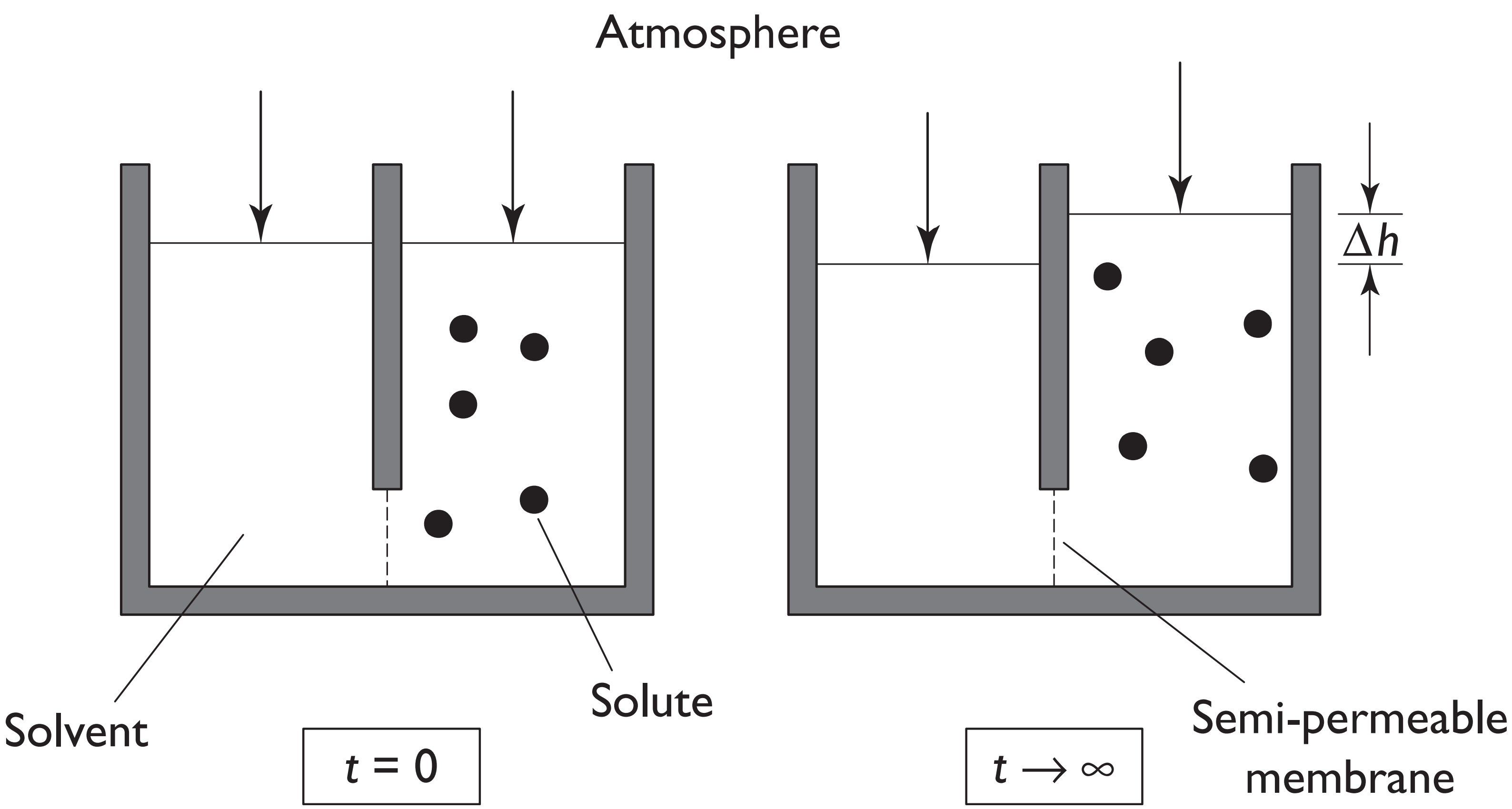
mantendo todos os Nj

Osmose



$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

Osmose



Pressão Osmótica, Π

$$\Pi = \rho g \Delta h$$