ENTROPY IN BIOLOGY

Charles S. Peskin

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Lecture 1 :

Ideal gas

Entropy of mixing

Ideal solution

Incompressible ideal solution

Osmotic pressure

Reference : Fermi, Thermodynamics

Ideal Gas

We assume the ideal gas law

(1)
$$P(T, V) = \frac{nkT}{V}$$

and also the existence of an entropy function $S(T, V)$ such that

(2)
$$T dS = dQ$$

in any reversible change

Here the independent variables are

T = temperature
V = volume

the constants are

n = # of molecules
k = Boltzmann's constant

and the functions are

$$P(T,V) = \text{pressure}$$

$$S(T,V) = \text{entropy}$$

and we also need

$$U(T,V) = \text{internal energy}$$

Finally,

$$dQ = \text{heat added to the system during any change}$$

$$dW = PdV = \text{work done by the system during any change}$$

By conservation of energy

(3)
$$dQ = dU + PdV$$

during any infinitesimal transformation. If the transformation is reversible

(4)
$$TdS = dU + PdV$$

Now consider separately changes in which $dV=0$ and $dT=0$. In terus way, we get

(5)
$$T\frac{\partial S}{\partial T} = \frac{\partial U}{\partial T}$$

(6)
$$T\frac{\partial S}{\partial V} = \frac{\partial U}{\partial V} + P$$

Differentiate (5) with respect to V and (6) with respect to T:

(7)
$$T\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 U}{\partial T \partial V}$$

(8)
$$\frac{\partial S}{\partial V} + T\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 U}{\partial T \partial V} + \frac{\partial P}{\partial T}$$

Subtracting (7) from (8) gives the result that

(9)
$$\frac{\partial S}{\partial V} = \frac{\partial P}{\partial T} = \frac{nR}{V}$$

Substituting (9) into (6) gives

(10) $\quad \dfrac{\partial U}{\partial V} = T\dfrac{\partial S}{\partial V} - P = \dfrac{nkT}{V} - P = 0$

Thus $U(T,V)$ actually depends only on T.

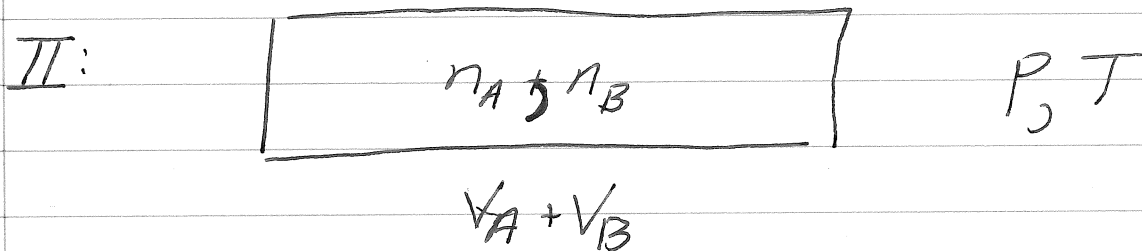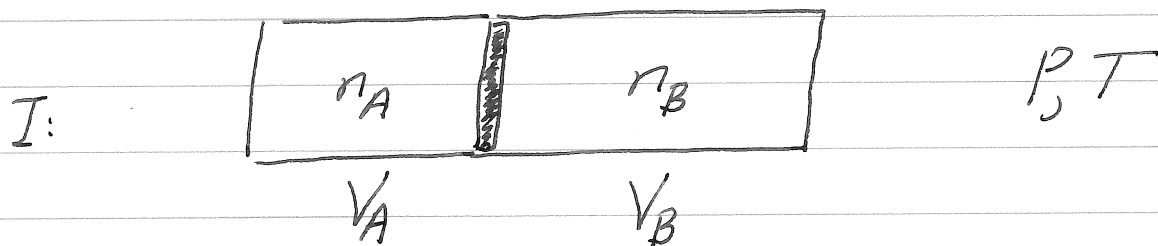Let $u(T)$ be the internal energy per molecule of the ideal gas. Then

(11) $\quad U(T,V) = n\,u(T)$

From (5) & (9),

(12) $\quad S(T,V) - S(T_0, V_0)$

$$= n\int_{T_0}^{T} \frac{1}{T'}\frac{du}{dT}(T')\, dT'$$

$$+ nk\, \log\frac{V}{V_0}$$

Entropy of mixing for ideal gasses.

We compare two situations

I:

n_A | n_B

V_A V_B

P, T

II:

n_A & n_B

$V_A + V_B$

P, T

$$P = \frac{n_A kT}{V_A} = \frac{n_B kT}{V_B}$$

$$\Rightarrow \begin{cases} PV_A = n_A kT \\ PV_B = n_B kT \end{cases}$$

$$\Rightarrow P(V_A + V_B) = (n_A + n_B) kT$$

$$\Rightarrow P = \frac{n_A + n_B}{V_A + V_B} kT$$

$$(S_A)_{II} - (S_A)_I = k\, n_A \log \frac{V_A + V_B}{V_A}$$

$$(S_B)_{II} - (S_B)_I = k\, n_B \log \frac{V_A + V_B}{V_B}$$

$$S_{II} - S_I = k\left(n_A \log \frac{V_A + V_B}{V_A} + n_B \log \frac{V_A + V_B}{V_B} \right)$$

$$= k\left(n_A \log \frac{n_A + n_B}{n_A} + n_B \log \frac{n_A + n_B}{n_B} \right)$$

$$= -k\left(n_A \log \frac{n_A}{n_A + n_B} + n_B \log \frac{n_B}{n_A + n_B} \right)$$

$$= -k\left(n_A \log X_A + n_B \log X_B \right)$$

$$= -k(n_A + n_B)\left(X_A \log X_A + X_B \log X_B \right)$$

Although the last line gives the _average_ entropy per molecule in the mixed state relative to the pure state at the same temperature and pressure in terms of the familiar formula

$$-k \sum_i X_i \log X_i$$

in which the X_i are like probabilities since their sum is _1_, the next-to-last line has an even simpler interpretation:

The entropy change for _each molecule_ of species i to move it from a pure state to a state where its mol fraction is X_i is

$$-k \log X_i$$

(and of course this can also be written as

$$k \log \left(\frac{1}{X_i} \right) \quad)$$

Remark:

The transition from $I \rightarrow II$ is an example of an irreversible process.

Although the entropy has increased, no work was done, and no heat was exchanged with the reservoir that maintains the temperature T. This is consistent with conservation of energy, since the internal energy of an ideal gas depends only on the temperature T, and it has not changed during the transition.

It is instructive to make the same transition from $I \rightarrow II$ in a reversible manner, and to see how much work can be done in the process

I)

II)
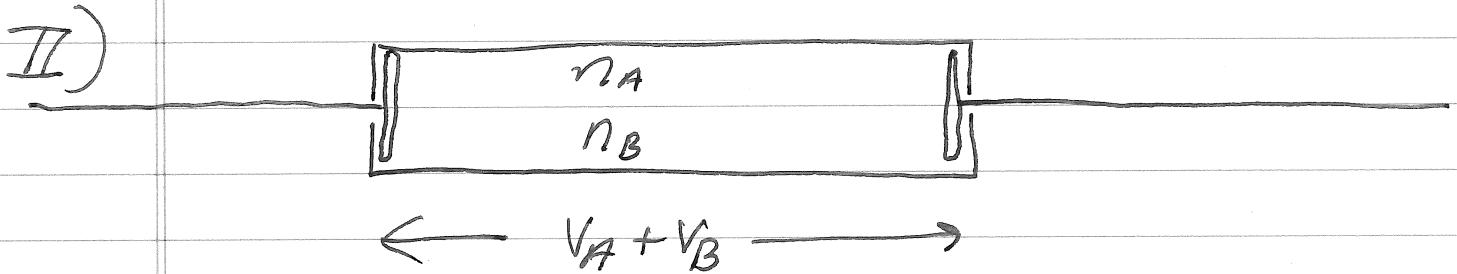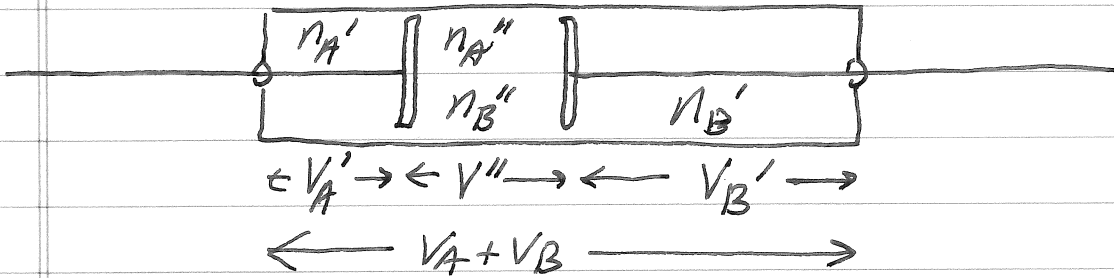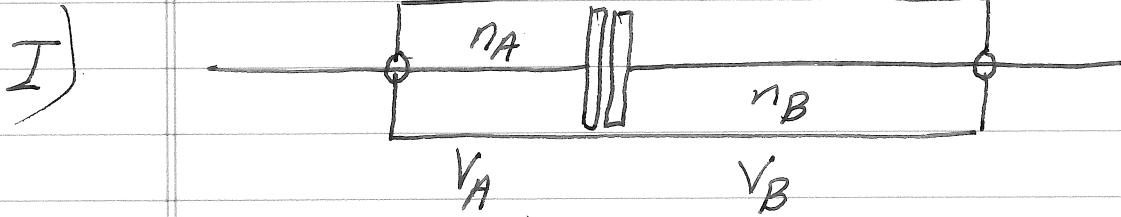
The piston on the left is permeable to A but not B

The piston on the right is permeable to B but not A

In the intermediate diagram above, the partial pressure of A is the same in the two left chambers, and the partial pressure of B is the same in the two right chambers. Therefore,

$$P_A = \frac{n_A kT}{V_A + V_B - V_B'} \quad, \quad P_B = \frac{n_B kT}{V_A + V_B - V_A'}$$

Since $T = $ constant,

$$dW = -P_A \, dV_B' - P_B \, dV_A'$$

$$= -\frac{n_A kT \, dV_B'}{V_A + V_B - V_B'} - \frac{n_B kT \, dV_A'}{V_A + V_B - V_A'}$$

$$W_{I \to II} = -\int_{V_B}^{0} \frac{n_A kT \, dV_B'}{V_A + V_B - V_B'} - \int_{V_A}^{0} \frac{n_B kT \, dV_A'}{V_A + V_B - V_A'}$$

$$= n_A kT \, \log\left(V_A + V_B - V_B'\right)\Big|_{V_B}^{0} - n_B kT \, \log\left(V_A + V_B - V_A'\right)\Big|_{V_A}^{0}$$

$$= n_A kT \, \log \frac{V_A + V_B}{V_A} + n_B kT \, \log \frac{V_A + V_B}{V_B}$$

Recall the assumption that on state I,

$$P = \frac{n_A kT}{V_A} = \frac{n_B kT}{V_B}$$

i.e., the two chambers are in pressure equilibrium at the start. Then

$$W_{I \to II} = n_A kT \log \frac{n_A + n_B}{n_A}$$

$$+ n_B kT \log \frac{n_A + n_B}{n_B}$$

$$= T \left(S_{II} - S_I \right)$$

Thus, the work done by the system is equal to T times the increase in entropy of the system. (Note that the change in the internal energy of the system is zero.) By conservation of energy, this

is also equal to the heat that flows into the system from the reservoir that maintains the temperature T. The reservoir thus has a lower entropy than before, and the entropy of the world has not changed during this reversible process.

(OPTIONAL)

<u>HW</u>: In the foregoing we assumed that the two gasses are at the same pressure initially. If they are not, we can still evaluate the change in entropy directly, or we can consider two steps (both at constant T):

First allow the partition to move without any mixing to equalize the pressures, and then proceed as above to allow mixing to occur. Show that the entropy change overall is the same either way. If the two steps are done reversibly, show that the work done is the same either way.

Ideal Solutions

Here we change to T, P as independent variables.

An ideal solution is a mixture in which energy and volume are additive

$$U(T, P, N) = \sum_i N_i \, u_i(T, P)$$

$$V(T, P, N) = \sum_i N_i \, v_i(T, P)$$

Note that a mixture of ideal gasses is an example of an ideal solution since the energy is additive

$$U(T, N) = \sum_i N_i \, u_i(T)$$

and since each component satisfies the ideal gas law

$$P_i \, V(T, P, N) = N_i \cdot kT$$

with its own partial pressure, and since

The partial pressures add up to the total pressure

$$P = \sum_i P_i = \frac{\sum_i N_i \, kT}{V(T,P,N)}$$

Thus

$$V(T,P,N) = \sum_i N_i \, \frac{kT}{P}$$

which is of the required form with

$$v(T,P) = \frac{kT}{P}$$

Remark

The terminology <u>ideal solution</u> is often used to mean the same thing as a <u>dilute solution</u>, and indeed one can use a Taylor series argument (Fermi) to show that a dilute solution is ideal, i.e., that it has the additivity property. Here, however, we define an ideal solution to be one with the above additivity, and then there is no requirement that the solution be dilute.

It remains to evaluate $S(T, P, N)$

This can be done as follows. For reversible changes, we have

$$T dS = dU + P dV$$

Considering separately changes in T with P = constant, and changes in P with T = constant, thus gives

$$T \frac{\partial S}{\partial T} = \frac{\partial U}{\partial T} + P \frac{\partial V}{\partial T}$$

$$T \frac{\partial S}{\partial P} = \frac{\partial U}{\partial P} + P \frac{\partial V}{\partial P}$$

Making use of the assumed additivity of the ideal solution, we can rewrite these equations as

$$T \frac{\partial S}{\partial T} = \sum_i N_i \left(\frac{\partial u_i}{\partial T} + P \frac{\partial v_i}{\partial T} \right)$$

$$T \frac{\partial S}{\partial P} = \sum_i N_i \left(\frac{\partial u_i}{\partial P} + P \frac{\partial v_i}{\partial T} \right)$$

Let
$$\sigma_i(T,P)$$

be the entropy per molecule of the pure substance i. It satisfies

$$T\frac{\partial \sigma_i}{\partial T} = \frac{\partial u_i}{\partial T} + P\frac{\partial v_i}{\partial T}$$

$$T\frac{\partial \sigma_i}{\partial P} = \frac{\partial u_i}{\partial P} + P\frac{\partial v_i}{\partial P}$$

Therefore, after dividing by T

$$\frac{\partial S}{\partial T}\bigg|_{P,N} = \sum_i N_i \frac{\partial \sigma_i}{\partial T}(T,P)$$

$$\frac{\partial S}{\partial P}\bigg|_{T,N} = \sum_i N_i \frac{\partial \sigma_i}{\partial P}(T,P)$$

and it follows that

$$S(T,P,N) = \sum_i N_i \sigma_i(T,P) + G(N)$$

Since $C(N)$ does not depend on (T, P), we can evaluate it by considering T so large and P so small that our solution becomes a mixture of ideal gasses, for which we have

$$S(T, P, N) = \sum_i N_i \, \sigma_i (T, P) - k \sum_i N_i \log X_i$$

where $X_i = N_i / \sum_J N_J$.
Thus

$$C(N) = -k \sum_i N_i \log X_i$$

And we have a formula for the entropy of and ideal solution

$$S(T, P, N) = \sum_i N_i \left(\sigma_i (T, P) - k \log X_i \right)$$

Incompressible ideal solution

For an ideal solution in the liquid state, it is often a good approximation to assume that v_i is constant, independent of (T, P). In that case

$$T \frac{\partial \sigma}{\partial T} = \frac{\partial u}{\partial T} \quad \Rightarrow \quad T \frac{\partial^2 \sigma}{\partial T \partial P} = \frac{\partial^2 u}{\partial T \partial P}$$

$$T \frac{\partial \sigma}{\partial P} = \frac{\partial u}{\partial P} \quad \Rightarrow \quad \frac{\partial \sigma}{\partial P} + T \frac{\partial^2 \sigma}{\partial T \partial P} = \frac{\partial^2 u}{\partial T \partial P}$$

so

$$\frac{\partial \sigma}{\partial P} = 0 \qquad \text{and} \qquad \frac{\partial u}{\partial P} = 0$$

Thus σ and u are both functions of T only, and these functions are related by

$$T \frac{\partial \sigma}{\partial T} = \frac{\partial u}{\partial T} \quad \Rightarrow \quad \sigma(T) - \sigma(T_0) = \int_{T_0}^{T} \frac{1}{T'} \frac{du}{dT}(T') dT'$$

Thus, for an incompressible ideal solution

$$U(T,P,N) = \sum_i N_i \, u_i(T) \qquad \text{(independent of } P)$$

$$V(T,P,N) = \sum_i N_i \, v_i \qquad \text{(independent of } T,P)$$

$$S(T,P,N) = \sum_i N_i \left(\sigma_i(T) - k \log X_i \right)$$
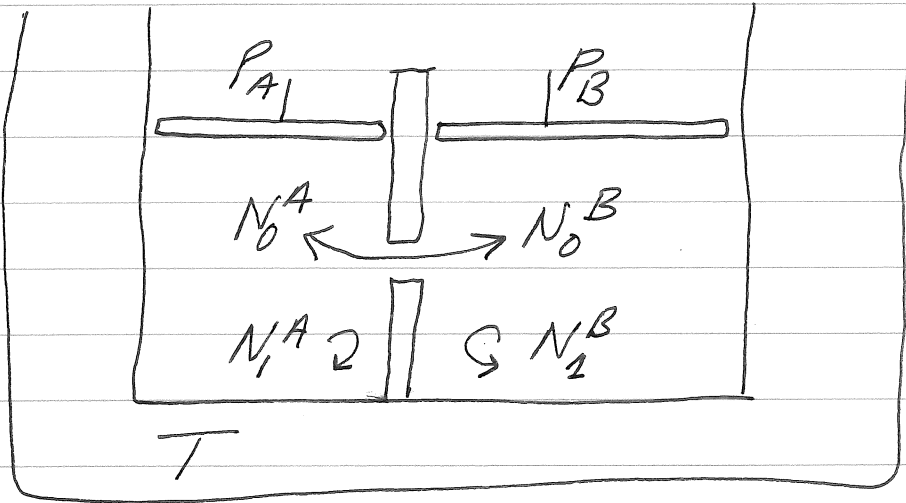
$$\text{(independent of } P)$$

where

$$X_i = N_i \Big/ \sum_j N_j$$

and

$$T \frac{d\sigma_i}{dT}(T) = \frac{du_i}{dT}(T)$$

Osmotic Pressure

$0 =$ solvent
$1 =$ solute

Suppose dN_0 molecules of solvent move
from $A \to B$ at constant T

$*$

$$dW = TdS \qquad \text{since } dU = 0$$

$$(P_B - P_A)\, \bar{v}_0\, dN_0 = T\, dN_0 \left(-k \log \frac{X_0^B}{X_0^A}\right)$$

$$P_B - P_A = \frac{kT}{\bar{v}_0} \log \frac{X_0^A}{X_0^B}$$

$*$ If the change is reversible, i.e., at equilibrium

The formula for dS in the foregoing seems to ignore the changes on mole fraction that occurs when dN_b molecules move from $A \rightarrow B$. Note however that

$$d \sum_i N_i \log X_i$$

$$= \sum_i dN_i \log X_i + \sum_i N_i \frac{dX_i}{X_i}$$

and the latter term is zero, since

$$X_i = \frac{N_i}{\sum N_j}$$

so

$$\sum_i N_i \frac{dX_i}{X_i} = \left(\sum_j N_j \right) \left(\sum_i dX_i \right)$$

and

$$\sum_i dX_i = d \left(\sum_i X_i \right) = d(1) = 0$$

We can rewrite the osmotic pressure law in terms of the concentrations of solute on the two sides of the membrane.

This is easier to do if we express concentration in terms of molality, i.e., the

number of molecules of solute per unit volume of solvent (not per unit

volume of solution, which would be molarity)

Thus we define

$$C_1 = \frac{N_1}{N_0 \upsilon_0} = \frac{X_1}{X_0 \upsilon_0} = \frac{1 - X_0}{X_0 \upsilon_0}$$

and solve for X_0:

$$X_0 = \frac{1}{1 + \upsilon_0 C_1}$$

This gives the osmotic pressure law in the form

$$P_B - P_A = \frac{kT}{v_0} \log\left(\frac{1 + v_0 C_1^B}{1 + v_0 C_1^A}\right)$$

If $X_1^A << X_0^A$ and $X_1^B << X_0^B$

Then $v_0 C_1^A << 1$ and $v_0 C_1^B << 1$

and we have

$$P_B - P_A = \frac{kT}{v_0}\left(v_0 C_1^B - v_0 C_1^A\right) = kT\left(C_1^B - C_1^A\right)$$

This looks just like the ideal gas law but note that here we have molality instead of molarity, and also the solution has to be dilute. For dilute solutions, however, molality and molarity are approximately the same.

Molality and Molarity are related as follows

$$C_1 = \frac{N_1}{v_0 N_0} \quad , \quad \bar{C}_1 = \frac{N_1}{v_0 N_0 + v_1 N_1}$$

$$= \frac{\frac{N_1}{v_0 N_0}}{1 + v_1 \frac{N_1}{v_0 N_0}} = \frac{C_1}{1 + v_1 C_1} \, ,$$

Therefore

$$\bar{C}_1 + v_1 C_1 \bar{C}_1 = C_1$$

$$\bar{C}_1 = C_1 (1 - v_1 \bar{C}_1)$$

$$C_1 = \frac{\bar{C}_1}{1 - v_1 \bar{C}_1}$$

Therefore, the osmotic pressure law in terms of the molarities is

$$P_B - P_A = \frac{kT}{v_0} \log \frac{1 + v_0 \dfrac{\bar{C}_2^B}{1 - v_1 \bar{C}_1^B}}{1 + v_0 \dfrac{\bar{C}_1^A}{1 - v_1 \bar{C}_1^A}}$$

$$= \frac{kT}{\left(\frac{v_0}{v_1}\right)v_1} \log\left(\frac{1+\left(\frac{v_0}{v_1}\right)\dfrac{v_1 \bar{C}_1^B}{1-v_1 \bar{C}_1^B}}{1+\left(\frac{v_0}{v_1}\right)\dfrac{v_1 \bar{C}_1^A}{1-v_1 \bar{C}_1^A}}\right)$$

Now take the limit $\dfrac{v_0}{v_1} \to 0$ with

$v_1, \bar{C}_1^B, \bar{C}_1^A$ all fixed. Then

$$P_B - P_A \to \frac{kT}{v_1}\left(\frac{\theta_1^B}{1-\theta_1^B} - \frac{\theta_1^A}{1-\theta_1^A}\right)$$

where

$$\theta_1^{A,B} = v_1 \bar{C}_1^{A,B} = \left(\text{volume fraction of solute}\right)^{A,B}$$

This limiting result can also be written as

$$P_B - P_A = \frac{kT}{v_1}\frac{\theta_1^B - \theta_1^A}{(1-\theta_1^B)(1-\theta_1^A)}$$

$$= \frac{kT(\bar{C}_1^B - \bar{C}_1^A)}{(1-\theta_1^B)(1-\theta_1^A)}$$

The above formula gives an excluded-volume correction to the standard osmotic pressure law for colloidal solute particles, i.e., for particles that are large in comparison to the solvent molecules.

On the other hand, we get the standard osmotic pressure law in this case if we use molality instead of molarity.