Biophysical Chemistry for Life Scientists

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Lecture 5

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1) Overheads
2) 40 copies stapled

Why do we need the Second Law?

First Law: $dE = dQ + dw$

- **relates heat input to and work done on a system, and the change in energy of the system**
- **merely a statement of conservation of energy**

Accordingly, the First Law does not say whether the process will occur; that is, tell us if a given process is spontaneous.

Second Law accomplishes this!

Second Law: $dS \geq DQ/T$

where DQ is the heat input to the system
and T is the absolute temperature

For an isolated system, one may immediately write $\Delta S_{\text{system}} \geq 0$

> 0, if the system has undergone a spontaneous process;

$= 0$, if the system has been at equilibrium;

< 0, if the process could only occur in the reverse direction.

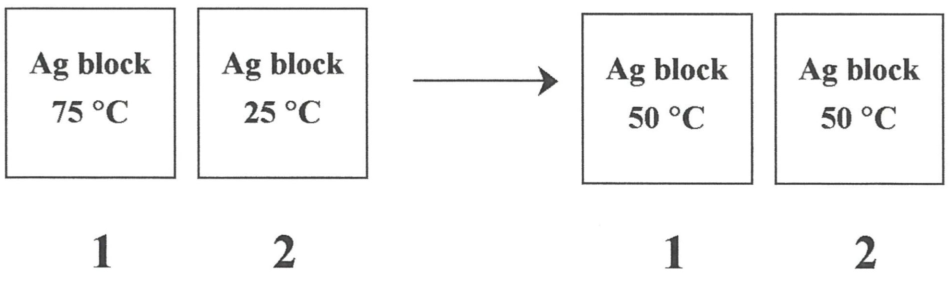
We shall illustrate this result by way of three examples:

(a) Heat flow between two silver blocks

(b) Melting of an ice block at 25 °C

(c) Isothermal expansion of perfect gas into a vacuum

Heat flow between two silver blocks



$$W_1 = 0$$

$$Q_1 = C_v(50 - 75)$$

$$= -25\ C_v$$

$$\Delta E_1 = Q_1 + W_1$$

$$= -25\ C_v$$

$$\Delta H_1 = -25\ C_v$$

$$W_2 = 0$$

$$Q_2 = C_v(50 - 25)$$

$$= 25\ C_v$$

$$\Delta E_2 = Q_2 + W_2$$

$$= 25\ C_v$$

$$\Delta H_2 = 25\ C_v$$

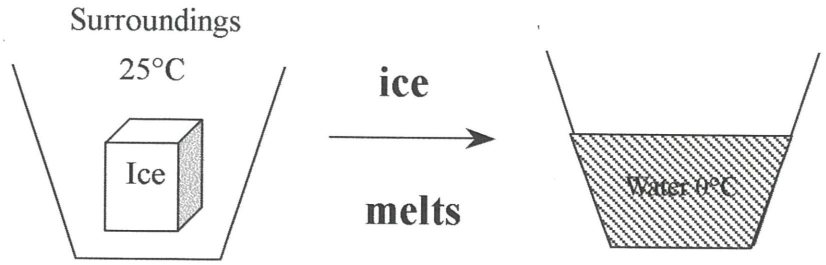
Therefore, $\Delta E_{process} = 0$

$\Delta H_{process} = 0$

But $\Delta S_{process} > 0$

We know from experience that the process will proceed from left to right, but not from right to left.

- **Melting of an ice block at 25 °C**



$$W_{ice} \cong 0 \qquad W_{air} \cong 0$$

$$Q_{ice} \cong \Delta H_{fusion} > 0 \qquad Q_{air} \cong \Delta H_{fusion} < 0$$

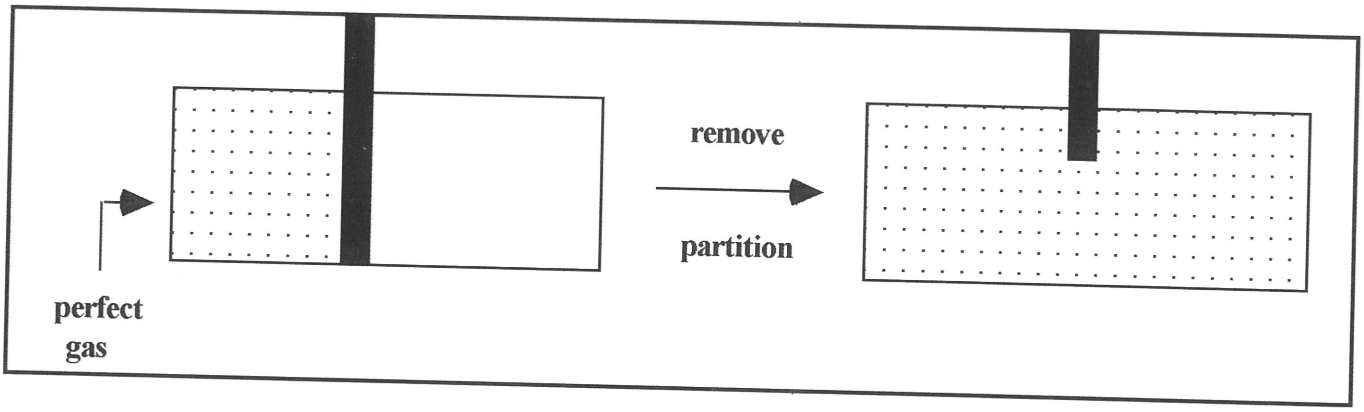
so that $\Delta E_{process} = Q_{ice} + W_{ice} + Q_{air} + W_{air}$

$$= \Delta H_{process} = 0$$

But $\Delta S_{process} > 0$

We know from experience that ice melts, but the spontaneous freezing of the water to form ice (the release of heat from the water at 0 °C to the surrounding air at 25 °C) does not occur.

- **Isothermal expansion of a perfect gas into a vacuum**



Temperature T

We know that $\Delta E_{process} = 0$ because $(\partial E/(\partial V)_T = 0$ for a perfect gas. Also, W = 0 and Q = 0 for this process. However. $\Delta S_{process} > 0$, as we have shown.

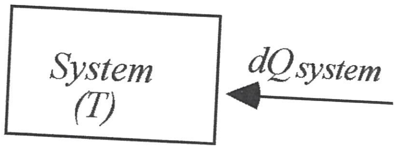
We know from experience that the reverse process does not occur.

The above processes all have $\Delta E_{process} = \Delta H_{process} = 0$, as they must, either (a) because we are including the system and its surroundings in the analysis, in which case, $\Delta E_{system} + \Delta E_{surroundings} = 0$ and $\Delta H_{system} + \Delta H_{surroundings} = 0$ always, because of conservation of

energy); or (b) the process does not entail a change in ΔE_{system} or ΔH_{system}, i.e., there is no ΔE_{system} or ΔH_{system} to drive the process forward; in other words, the process is entropy driven.

Concept of free energy. Free energy change as a criterion for spontaneity.

- **Consider a process:**



According to second law,

$$dS_{system} \geq \frac{dQ_{system}}{T_{system}}$$

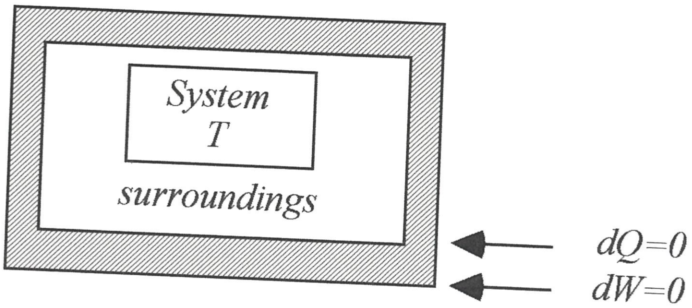
note dQ_{system} **could be negative or positive**

where $= dQ/T$ if the process is reversible

$> dQ/T$ if the process is irreversible

In order to establish spontaneity, we need to evaluate ΔS_{system} between initial and final state, and also $\int_i^f \frac{dQ_{system}}{T_{system}}$ and compare. Analysis is clumsy; often it is difficult to evaluate $\int_i^f \frac{dQ_{system}}{T_{system}}$.

A way out of this difficulty is to enclose the system with a surrounding and isolate it!



Then $dS_{system} + dS_{surroundings} \geq 0$ **=0 for a reversible process**

>0 for an irreversible process

or $\Delta S_{system} + \Delta S_{surroundings} \geq 0$

But we must evaluate ΔS_{system} and $\Delta S_{surroundings}$ and compare the two. In any case, from this analysis, it follows that

$\Delta S \geq 0$ **for a process involving an isolated system.**

$= 0$ **for a reversible process or an isolated system that has been at equilibrium**

> 0 **for an irreversible or spontaneous process.**

Why free energy?

The concept of free energy was introduced so that we could just focus on the system itself and alone.

- **Helmholtz introduced the Helmholtz free energy A:** $A \equiv E - TS$

- **Gibbs introduced the Gibbs free energy G:**

$$G \equiv H - TS$$

Both A and G are extensive property of the system, like E, H, and S.

It turns out ΔA and ΔG provide useful criteria for spontaneity of a process under certain conditions (shown in detail later).

(1) For a process taking place at constant T and V:

$dA = dw$ **for reversible process or system at equilibrium**
$dA < dw$ **for spontaneous process**

If $dw = 0$**, i.e., no pV or useful work (constant T and V and** $dw' = 0$**)**

$$\left.\begin{array}{ll}\text{then} & dA \le 0 \\ \text{or} & \Delta A_{system} \le 0\end{array}\right\} \begin{array}{l} = 0 \text{ for reversible process or system at equilibrium} \\ < 0 \text{ for an irreversible or spontaneous process}\end{array}$$

(2) For a process taking place at constant T and P (P = Pext)

$dG = dw'$ **for reversible process or system at equilibrium**
$dG < dw'$ **for spontaneous or irreversible process**

If $dw' = 0$**, i.e., no useful work being carried out,**

$$\left.\begin{array}{ll}\text{then} & dG \le 0 \\ \text{or} & \Delta G_{system} \le 0\end{array}\right\} \begin{array}{l} = 0 \text{ for reversible process or system at equilibrium} \\ < 0 \text{ for an irreversible or spontaneous process}\end{array}$$

Thus for a system undergoing (1) an isothermal process at constant volume, or (2) an isothermal

process at constant external pressure, the criteria for spontaneity is given by ΔA_{system} or ΔG_{system} and the sign of the changes in these state functions, if no work is done on the system in (1), and no useful work is done on the system in (2). Note that these are the very processes that physicists, chemists, and biologists are dealing with in general. Thus, we may conclude that, for these kinds of processes, other factors being equal:

(1) a system will proceed toward a state of lower energy or enthalpy; and
(2) it will also tend toward a state of greater entropy or probability. For a process where the two contributions to the "driving force" are counteracting one another, a compromise is reached.

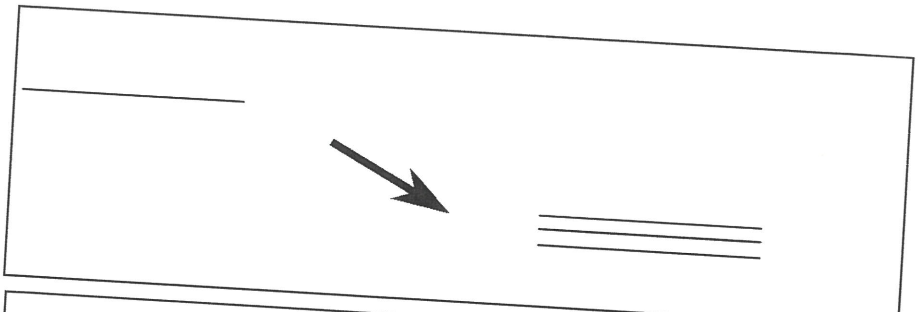
Accordingly, we can divide chemical and biological processes into the following types, because we may write under isothermal conditions (at constant T):

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

Initial state **Final state**

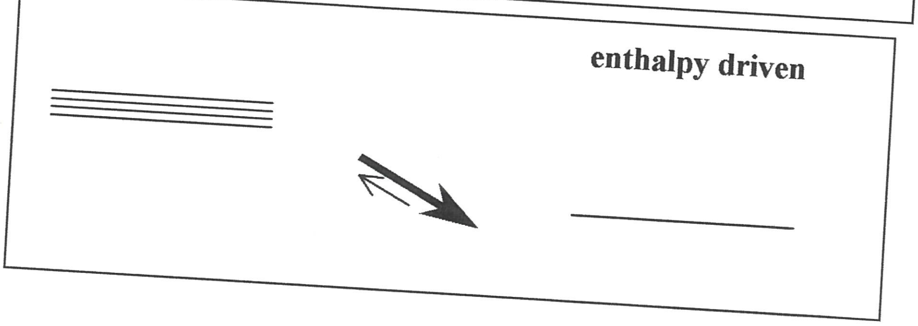
(A)

The general case



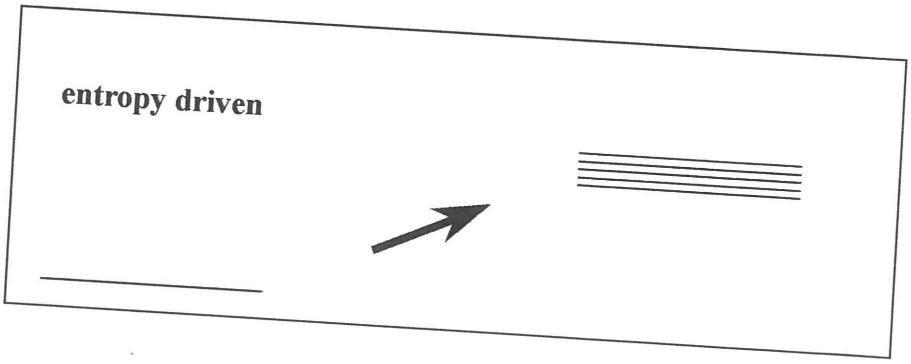
(B)

An enthalphy driven process



(C)

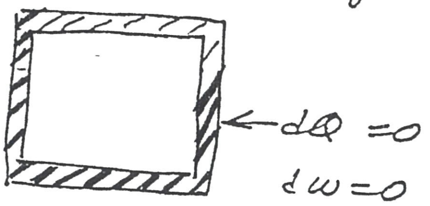
An entropy driven process



In the following pages, we shall derive the above results.

Criteria for Equilibrium and Directionality of a Process (Spontaneity)

(1) Isolated system (closed) of course



$$dS \geq \frac{dQ}{T}$$

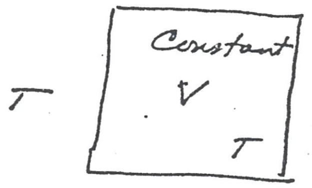
Condition for spontaneity

$dS = 0$ if system is at equilibrium

& $dS > 0$ gives the direction of process

or $\int_{\text{initial state}}^{\text{final state}} dS = \Delta S > 0$

(2) Constant T and V system (closed)



$$dS \geq \frac{dQ}{T}$$

. one equation for system

or $dS - \frac{dQ}{T} \geq 0$

. one equation for surrounding

Substitute First Law for dQ: $(dE = dQ + dW)$

$$dS + \frac{(-dE + dW)}{T} \geq 0$$

→ Introduce new state function A ≡ Helmholtz free energy

$$\boxed{A = E - TS}$$ property of system!

or $E = A + TS$

$\therefore$ $dE = dA + TdS + SdT$

Substituting above,

$$dS + \frac{-dA - TdS - SdT + dw}{T} \geq 0$$

or $\cancel{TdS} - dA - \cancel{TdS} - SdT + dw \geq 0$

i.e., $-dA - SdT + dw \geq 0$

→ <u>at constant T,</u>

we have $-dA + dw \geq 0$

or

$dA = dw$	for equilibrium
$dA < dw$	for criteria for direction of process.

→ Special condition of no work, i.e., $dw = 0$
no pV work $\Rightarrow$ V constant

Then
$$\boxed{\begin{array}{ll} dA = 0 & \text{equilibrium} \\ dA < 0 & \text{directional criteria} \end{array}}$$

$\Delta A = 0$

$\Delta A < 0$

↑

integrate from initial to final states

if T constant

V constant

& no other work

Helmholtz takes into consideration

→ Energy change & Entropy change

3) Constant T and P system.

Again start with
$$dS + \frac{(-dE + dw)}{T} \geq 0$$

Introduce $G \equiv$ Gibbs Free Energy

$$\boxed{G \equiv A + PV = E - TS + PV}$$

new state function G

or
$$E = G + TS - pV$$

&
$$dE = dG + TdS + SdT - pdV - Vdp$$

Substituting,

$$dS + \frac{-dG - TdS - SdT + pdV + Vdp + dw}{T} \geq 0$$

or
$$\frac{1}{T}(\cancel{TdS} - dG - \cancel{TdS} - SdT + pdV + Vdp + dw) \geq 0$$

i.e.,
$$\frac{1}{T}(-dG - SdT + pdV + Vdp + dw) \geq 0$$

If reversible pV work, then $dw = dw' - p\,dV$

dw' = all other work except reversible pV work

generally the case when chemists run a reaction under conditions $P_{system} = P$; also generally true for biological systems

Then

$$-dG - S\,dT + V\,dp + dw' \geq 0$$

Constant T & P

$$-dG + dw' \geq 0$$

or

$$\boxed{\begin{array}{ll} dG = dw' & \text{for equilibrium} \\ dG < dw' & \text{for direction of process} \end{array}}$$

→ Special case $dw' = 0$

Then

$$\boxed{\begin{array}{ll} dG = 0 & \text{for equilibrium} \\ dG < 0 & \text{for direction of process} \end{array}}$$

Constant T, P
and no work other than reversible
PV work.

Integrate from initial to final state

$\Delta G = 0$ for process at equilibrium

$\Delta G < 0$ for irreversible process

System	Work(?)	System at equilibrium	Reversible process	Spontaneous process
) Isolated	0	$dS=0$	$\Delta S=0$	$\Delta S>0$
) Isothermal at temp. T	PV work plus w_{useful}	$dA = dw_{total}$	$\Delta A = w_{total}^{rev}$	$\Delta A < w_{total}$ (or $-w_{total} < -\Delta$
	PV work only	$dA = -p\,dV$	$\Delta A = -\int p\,dV$	$\Delta A < -\int p_{ex}\,dV$
	constant V but w_{useful}	$dA = dw_{useful}$	$\Delta A = w_{useful}^{rev}$	$\Delta A < w_{useful}$ (or $-w_{useful} < -$
	Constant V & no w_{useful}	$dA = 0$	$\Delta A = 0$	$\Delta A < 0$
3) Isothermal at temp T and p	w_{useful}	$dG = dw_{useful}$	$\Delta G = w_{useful}^{rev}$	$\Delta G < w_{useful}$ (or $-w_{useful} \le -$
	no useful work	$dG = 0$	$\Delta G = 0$	$\Delta G < 0$

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a $-w_{total} < -\Delta A = -w_{total}^{rev}$ $\therefore$ $-\Delta A$ is maximum work that can be extracted by process at constant T

b $-w_{u\text{[illegible]}ul} < -\Delta G = -w_{useful}^{rev}$ $\therefore$ $-\Delta G$ is maximum useful that can be extracted from syste[illegible]y process at constant T and p.