CHEMISTRY 24a
Winter Quarter 1997
Instructor: Chan
Lecture: 6
Date: January 22, 1997

$S_{sys.} = k_B \ln \Omega$
↳ system degeneracy
of $\Psi_{sys.}$ for a given E, V
or T, V

Reading Assignment

Eisenberg & Crothers: Chapter 4 (continued)

Criteria for Spontaneity

There are two important considerations: 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. To illustrate these principles, I offer the following examples.

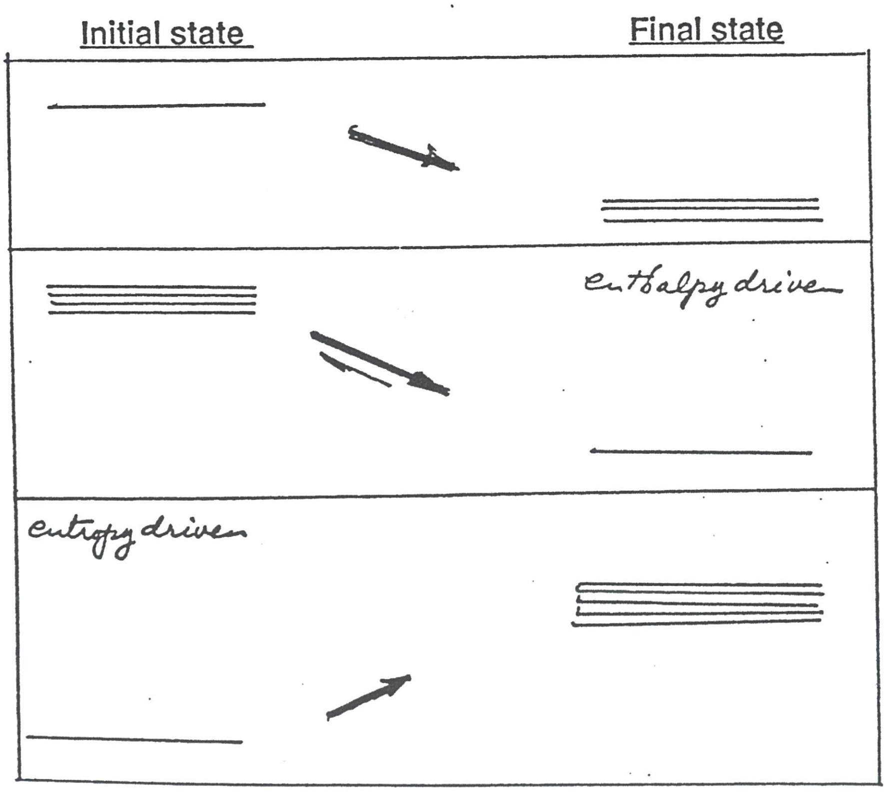
System states (ie, not quantum states).

E or H of system ↑

(A)

(B)

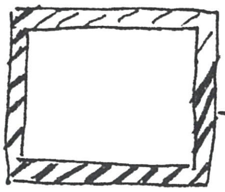
(C)



Criteria for Equilibrium and Directionality of a Process

(Spontaneity)

(1) Isolated system (closed) of course



$\leftarrow dQ = 0$

$dW = 0$

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

Condition for spontaneity

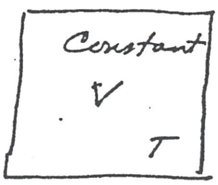
$dS = 0$ if system is at equilibrium

& $dS > 0$ gives the direction of process
i.e., if $dS > 0$, then process is spontaneous.

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

(2) Constant T and V system (closed)

no mass transfer



T

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

. one equation for system

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

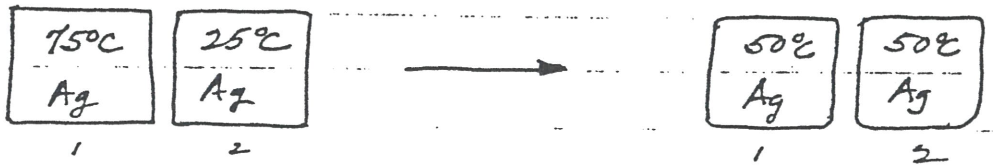
. one equation for surrounding

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

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

→ Illustrate the point by way of several examples.

(1) Heat flow between silver blocks (same mass)



$W = 0$

$Q_1 = C_v(50-75)$
$= -25C_v$

$\Delta E_1 = -25C_v$
ΔH_1

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

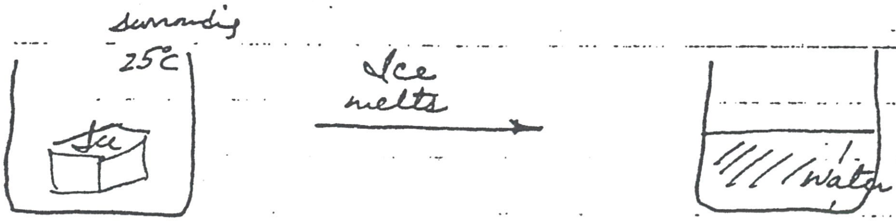
$\Delta E_2 = 25C_v$
ΔH_2

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

We know from experience that the process will proceed from left to right, but <u>not</u> from right to left

Both the forward process as well as the backward process satisfies First Law.

(2)

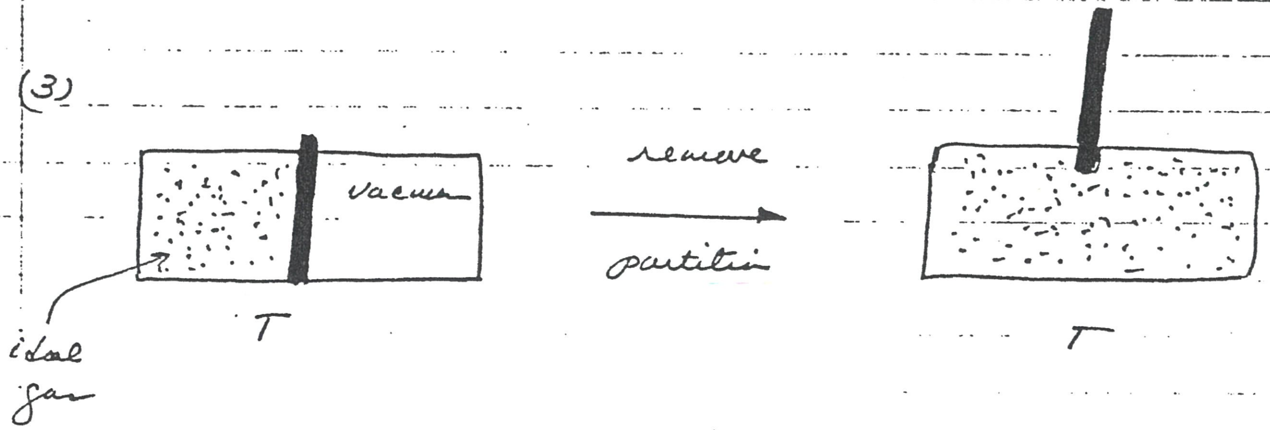


$W \simeq 0$

$Q_{ice} = \Delta H_{fusion} > 0$

From experience, we know that ice melts, but spontaneous freezing of the water to form ice releasing heat to surrounding does not take place.

(3)



$\Delta E = 0$ because $\left(\frac{\partial E}{\partial V}\right)_T = 0$ for ideal gas

$Q = 0$

$w = 0$

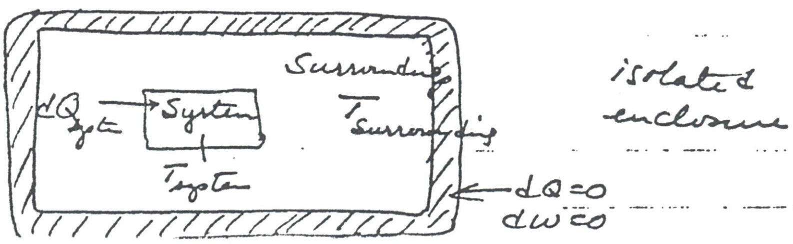
From experience, we know that reverse process does not occur.

Need a prescription, or set of criteria, that one can use to predict whether a process is spontaneous or not.

The Second Law of Thermodynamics leads to such a set of Criteria.

Statement of the Second Law

Take from Eisenberg and Crothers p. 87



Suppose a spontaneous process cont occurs in the system. Suppose also that the system plus its surroundings are isolated

Then

(1) For a small amount of heat dQ_{rev} delivered to the system in a reversible process at temperature T, it follows that the differential

$$\frac{dQ_{rev}}{T_{system}} = \frac{dQ_{rev}}{T}$$

is an exact differential (of a property of the system).

If this quantity is an exact differential, the ca define a state function $S(T, V, N)$ such that

$$dS_{system} = \frac{dQ_{rev}}{T_{system}} \quad \text{or} \quad dS = \frac{dQ_{rev}}{T}$$

→ It turns out S is the entropy function (entropy from the Greek words en (in) and trope (turning), meaning "to give direction"). This property of state was first realized by German physicist Rudolf Clausius in 1850.

→ $\frac{1}{T}$ is an integrating factor for dQ_{rev}

An integrating factor in mathematics is a factor which when multiplied by an inexact differential converts the product into an exact differential

In this instance, the integrating factor is reciprocal of absolute

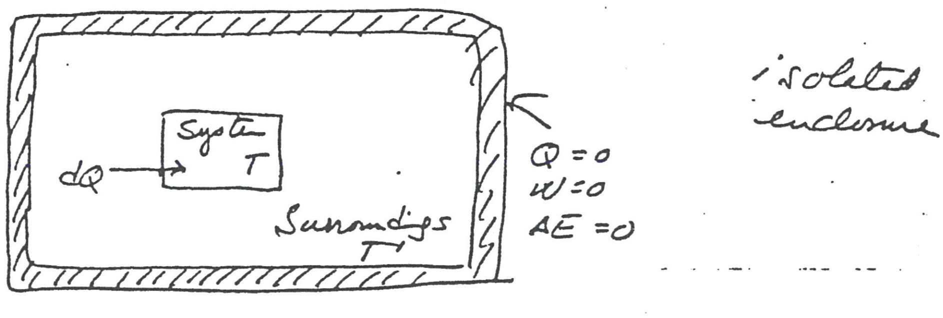
(2) For an irreversible process,

$$dS_{system} > \frac{dQ_{irr}}{T_{system}}$$ (i.e., heat input into system during irreversible process $< T_{system}\, dS_{system}$)

(3) From (2), it follows that for a <u>spontaneous process</u>, the total entropy change of the isolated enclosure is positive; i.e.,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} > 0$$ always irreversible

<u>Illustrate above concepts assuming that there is only transfer of heat from surroundings to system</u>



(1) <u>Reversible</u> heat transfer (process)

$T' = T$

dQ_{system} = heat input into system $= dQ_{rev}^{system}$

$dQ_{surroundings} = -dQ_{system}$ = heat absorbed by surroundings $= -dQ_{rev}^{system}$

$$dS_{system} = \frac{dQ_{rev}^{system}}{T_{system}} = \frac{dQ_{rev}^{system}}{T}$$

$$dS_{surroundings} = \frac{dQ_{rev}^{surroundings}}{T} = -\frac{dQ_{rev}^{system}}{T'} = -\frac{dQ_{rev}^{system}}{T}$$

$$dS_{Total} = dS_{system} + dS_{surrounding}$$

$$= \frac{dQ_{rev}^{system}}{T} - \frac{dQ_{rev}^{system}}{T} = 0$$

$\therefore \ \Delta S = 0$

Therefore, the total entropy change for the above reversible process is zero.

(2) Heat transfer when the temperatures of the system T and of the surrounding T' are not equal.

Let's assume that $dQ = dQ_{rev}$ is removed from the surroundings at temperature T' by a reversible path and $dQ = dQ_{rev}$ is added to the system at temperature T, again by a reversible path.

$$dQ_{system} = dQ_{rev}$$

$$dQ_{surrounding} = -dQ_{rev}$$

Then $dS_{total} = dS_{system} + dS_{surrounding}$

$$= \frac{dQ_{rev}}{T} - \frac{dQ_{rev}}{T'} = dQ_{rev}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

For a spontaneous process, according to Second Law,

$dS_{total} > 0$,

Then $dQ_{rev}\left(\frac{1}{T}-\frac{1}{T'}\right) > 0$

<u>Two cases</u>

(a) Surroundings <u>hotter than system</u>, $(T' > T)$

Then $\left(\frac{1}{T}-\frac{1}{T'}\right) > 0$

so that [redacted] $dQ_{rev} > 0$

or heat flows from surroundings to system.

(b) Surroundings colder than system $(T' < T)$

Then $\left(\frac{1}{T}-\frac{1}{T'}\right) < 0$

so that $dQ_{rev} < 0$

or heat flows from system to surroundings.

<u>Inescapable conclusion</u>

Heat flow from high to low temperature is predicted by second law