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By MARK LANDLER

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By EDMUND L. ANDREWS

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By ELISABETH ROSENTHAL

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Using the second law to define whether a process is spontaneous

$\Delta S \geq 0$ **for spontaneous events in isolated systems**

$\Delta S = 0$ for reversible processes at equilibrium

$\Delta S > 0$ for irreversible processes

$\Delta S < 0$ for non-spontaneous processes, highly unlikely

If system is not isolated, we can restate the second law:

The sum of the system and surroundings is greater than or equal to zero.

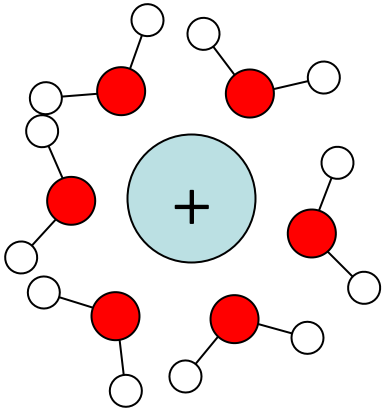
How does entropy drive processes?

1) Charge neutralization in a solvent

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \quad \overline{\Delta S}^o = 148\ Jmole^{-1}K^{-1}$$

$$HC_2O_4^-(aq) + OH^-(aq) \rightarrow C_2O_4^{2-}(aq) + H_2O(l) \quad \overline{\Delta S}^o = -23\ Jmole^{-1}K^{-1}$$

In the first case, the charge is neutralized, while in the second case, there is charge transfer but no neutralization.

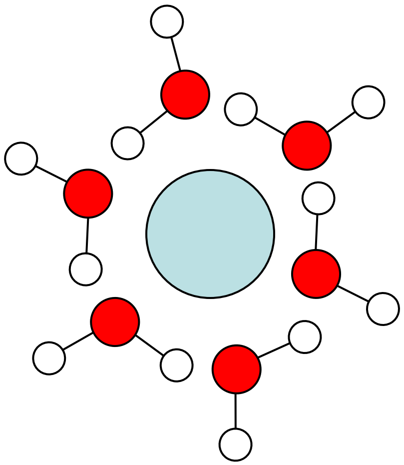


Binding of Netropsin by polydA-polydT

$$\overline{\Delta S}^o = 141\ Jmole^{-1}K^{-1}$$

2) Hydrophobic entropy

$$C_3H_8(l) \rightarrow C_3H_8(aq) \qquad \overline{\Delta S_{298K}}^{o} = -80\ Jmole^{-1}K^{-1}$$



We have learnt that we can calculate ΔS for an isolated system and determine whether a process is spontaneous or not.

It would be useful to define criteria for spontaneous changes for useful lab conditions such as constant T and P and constant T and V.

Let's start by seeing how entropy contributes to internal energy and enthalpy.

Defining criteria for spontaneous reversible processes assuming PV work

Energy	Equation	Criterion for spontaneous process	Equilibrium of a process
Internal energy $dU = dq + dw$	$dU = TdS - PdV$	$\left(dU\right)_{S,V} \leq 0$	$\left(dU\right)_{S,V} = 0$
Enthalpy $H = U + PV$	$dH = TdS + VdP$	$\left(dH\right)_{S,P} \leq 0$	$\left(dH\right)_{S,P} = 0$
Helmholtz Free Energy $A = U - TS$	$dA = -SdT - PdV$	$\left(dA\right)_{T,V} \leq 0$	$\left(dA\right)_{T,V} = 0$
Gibbs Free Energy $G = U + PV - TS$	$dG = -SdT + VdP$	$\left(dG\right)_{T,P} \leq 0$	$\left(dG\right)_{T,P} = 0$

I) Internal energy

$$dU = dq + dw$$ → **First Law**

$$TdS \geq dq$$ → **Second Law**

Note: The equality holds for only reversible processes

Step I: Let's consider only reversible and PV work,

Substituting, $dq = TdS$ and $dw = -PdV$ into the first law,

$$dU = TdS - PdV$$

Step II

Combining the first and second laws:

$$dU \leq TdS - PdV$$

Criterion for spontaneity:

$$\left(dU\right)_{S,V} \leq 0$$

A reversible process is spontaneous when the change in internal energy is zero for constant entropy and volume

II) Enthalpy

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

For reversible processes and PV work:

$$dH = TdS + VdP$$

We have used the expression that we derived for *dU* in the earlier slide

Combining the first and second laws:

$$dH \leq TdS + VdP$$

Criterion for spontaneity:

$$\left(dH\right)_{S,P} \leq 0$$

A reversible process is spontaneous when the change in enthalpy is zero for constant entropy and pressure.

From the above discussions, if we want to find whether a particular process is spontaneous we can set the lab conditions to constant T or V and then to constant S. Not very easy to do the latter!

Let’s define some more energies

III) Helmholtz Free Energy

→ Useful quantity for geochemists

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

For reversible processes and PV work:

$$dA = TdS - PdV - TdS - SdT$$

$$\boxed{dA = -PdV - SdT}$$

Combining the first and second laws:

$$dA \leq -SdT - PdV$$

Criteria for spontaneity:

$$(dA)_{V,T} \leq 0$$

III) Gibbs Free Energy

$$G = H - TS = U + PV - TS$$

$$dG = dH - TdS - SdT$$

For reversible processes and PV work:

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

Combining the first and second laws:

$$dG \leq -SdT + VdP$$

Criteria for spontaneity:

$$(dG)_{P,T} \leq 0$$

Helmholtz and Gibbs Free Energy and other kinds of work

Helmholtz free energy is the **maximum amount of total work ($w_{PV} + w_{non\text{-}pV}$) done by the system on the surroundings** at constant T.

Gibbs free energy is the **maximum amount of non-PV work done by the system on the surroundings** at constant T.

Gibbs Free Energy and Non-PV work

$$G = H - TS = U + PV - TS$$

$$dG = dq - \cancel{PdV} + dw_{non-PV} + \cancel{PdV} + VdP - TdS - SdT$$

Using the fact that $TdS \geq dq$ in the above expression

$$dG \leq VdP + dw_{non-PV} - SdT$$

For an isothermal and constant pressure process, we see that

$$dG \leq dw_{non-PV}$$

In other words, Gibbs free energy is the maximum work the system can do on the surroundings at constant T and P.

Helmholtz Free Energy and work

$$A = U - TS$$

$$dA = dq + dw_{PV} + dw_{non-PV} - TdS - SdT$$

Using the fact that $TdS \geq dq$ in the above expression

$$dA \leq dw_{PV} + dw_{non-PV} - SdT$$

For an isothermal process, we see that

$$dA \leq dw_{total}$$

In other words, Helmholtz free energy is the total maximum work the system can do on the surroundings at constant T.