Entropy

G=H-TS

1st law: $\Delta U = q - w$
Hear capacity: $C = q/\Delta T$

A new State Function: $$\Delta S = \frac{q_{rev}}{T}$$

Rudolf Clausius

CLASSICAL THERMODYNAMICS

study of *macroscopic/thermodynamic* properties of systems: *U, T, V, P, ...*

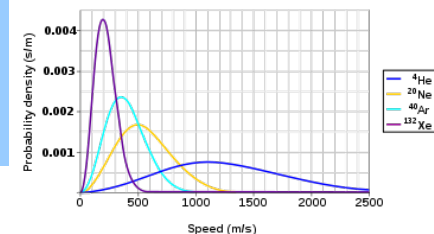*Ludvig Boltzmann*
1844-1906

$$S = k \ln N$$

STATISTICAL THERMODYNAMICS

establishing relationships between *microstates* and *macrostates*

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases

Enthalpy–Entropy Compensation in Drug–Receptor Binding

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The thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) of the drug–receptor binding equilibrium derived from equilibrium constant measurements at different temperatures and van't Hoff plots are reviewed. The analysis involves 186 independent experiments performed on 136 ligands binding to 10 biological receptors and, for comparison, to DNA and to two different enzymes. $\Delta H°$ and $\Delta S°$ values correlate according to the regression equation $\Delta H°$ (kcal mol^{-1}) = $-9.5 + 278\Delta S°$ (kcal K^{-1} mol^{-1}) with a correlation coefficient of 0.981. The correlating equation is of the form $\Delta H° = \beta\Delta S°$ and is expected for a case of enthalpy–entropy compensation with a compensation temperature $\beta = 278$ K. The $\Delta H–\Delta S$ correlation is carefully examined in terms of transmission of the experimental errors and of the representativeness of the experimental sample utilized. The correlation can be considered a true physical constraint for which, in spite of the relatively wide intervals of $\Delta H°$ and $\Delta S°$ allowed, the drug–receptor dissociation constant, K_D, can never be smaller than some 10 pM. The physicochemical origin of the $\Delta H–\Delta S$ compensation is probably related to an intrinsic property of the hydrogen bond, which is the main force determining the association of the participants (drug, receptor binding site, water) in the drug–receptor binding equilibrium.

Entropy as a measure of number of states

Log (W) function (where W is the number of states) makes Entropy additive and extensive

Entropic Botzmann by Les Dutton, PhD

Entropy : counting microstates

- **All alternative states of a system have the same energy U**

- A **macro-state** (eg gas or liquid) consists of N **microstates**

- **Micro**states are combinaitons of *molecular microstates* (n_{micro})
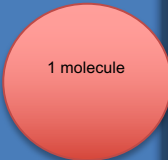
$$S = k_B \ln N_{microstates}$$

$$N_{for N_A molecules} = n^{N_A}$$

$$\ln a^x = x \ln a$$

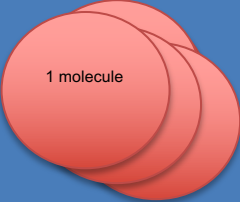$$S_{mole} = k_B \ln N = k_B N_A \ln n = R \ln n$$

Phase A

$n_{micro}=1$

1 molecule

- Phase B

$n_{micro}=10$

1 molecule

$$\Delta S_{AB}^{mole} = R \ln 10$$

Classical Entropy and Units

$$\Delta S = \frac{q}{T}$$

Entropy **Change** of a **Revers**ible Process =

Small Heat over **Absolute** Temperature

- Units of ∆S: **Joule/K** (or cal/K)

- Warnings: The units of Entropy are the same as Heat Capacity, however ∆S and C are totally different:

$$C = \frac{q}{\Delta T}$$

Heat Capacity of material =

Heat over Small Temperature **Change**

Entropy Change in an Irreversible Process

> ## *the Second Law of Thermodynamics*
> ### $\Delta S \geq 0$: in an isolated system S is increasing as it is reaching its equilibrium maximum value

- For an *irreversible* transition from state *A* to state *B*: $\int_A^B \dfrac{dq}{T} < \int_A^B \dfrac{dq_{rev}}{T} = \Delta S$

- *Irreversible $\Leftrightarrow$ spontaneous $\Leftrightarrow$ no work required $\Leftrightarrow \Delta U = q$*

Clausius: "No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature"

Kelvin: "No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work"

Entropy Changes in Specific Processes

- *Changes in volume or pressure* (e.g. in isothermal expansion of ideal gas). *Larger volume, more space microstates, N~V, S ~ lnV*

- *Changes in temperature* (illustrated by isobaric heating of ideal gas)   **PV=nRT** . *More microstates for energy values ~ T. N ~ T   S ~ lnT*

- *Phase changes* (at the transition temperature)

- Entropy of mixing (bigger volume for each molecule)

Entropy. Gas. Classical method: S (Volume) at T=const

T=const
ΔU=0, w=q

Increase in entropy

V_A

V_B
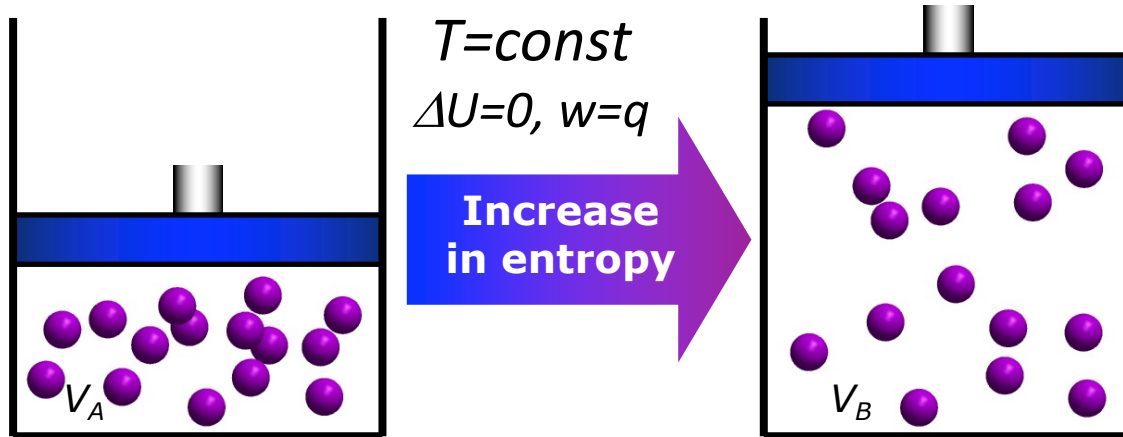
$$S = nR \cdot \ln V$$

$$\Delta S_T = nR \cdot \ln \left(\frac{V_B}{V_A} \right)$$

Classical Derivation (optional).   *PV = nRT*

- Consider ideal gas *isothermally expanding* from V_A to V_B . *ΔU = 0* because the internal energy for ideal gas only depends on the temperature

- As ΔS does not depend on path, choose a *reversible* path

- Entropy change:
$$\Delta S = \int_{V_A}^{V_B} \frac{dq_{rev}}{T} = \frac{1}{T} \int_{V_A}^{V_B} dq_{rev} = \frac{1}{T} \int_{V_A}^{V_B} PdV = \int_{V_A}^{V_B} \frac{nR}{V} dV = nR \ln(V) \Big|_{V_A}^{V_B}$$

$$q_{rev} = w = nRT \cdot \ln \left(\frac{V_B}{V_A} \right) \quad \Rightarrow \quad \boxed{\Delta S_T = nR \cdot \ln \left(\frac{V_B}{V_A} \right) = -nR \cdot \ln \left(\frac{P_B}{P_A} \right)}$$

Entropy. Gas. S(Temperature), P=const
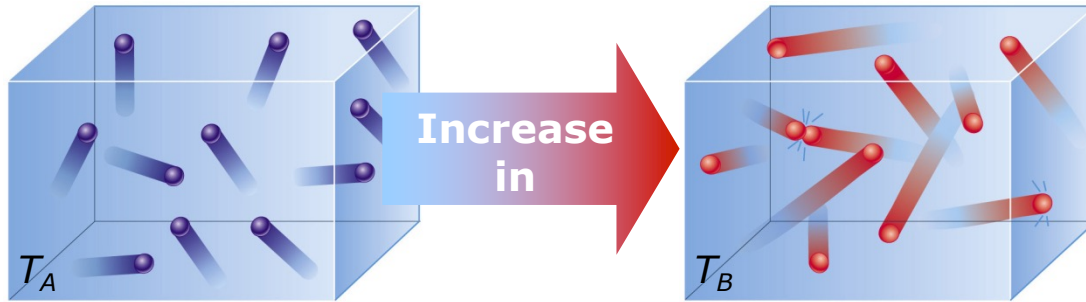
$$S = C_P \cdot \ln T$$

$$\Delta S_T = C_P \cdot \ln\left(\frac{T_B}{T_A}\right)$$

Classical Derivation (optional)

- Consider ideal gas *heating* from T_A to T_B at *constant pressure* or any other system where C_p does not change between T_A and T_B

- As ΔS does not depend on path, choose a *reversible* path:

$$dq_{rev} = C_P\, dT$$

- Entropy change:
$$\Delta S = \int_{T_A}^{T_B} \frac{dq_{rev}}{T} = \int_{T_A}^{T_B} C_P \frac{dT}{T} \quad \text{note}: \int \frac{dx}{x} = \ln x$$

- If $C_P \sim$ constant
- Note for n moles $C_P = nC_P^m$

$$\boxed{\Delta S_P = C_P \int_{T_A}^{T_B} \frac{dT}{T} = C_P \ln \frac{T_B}{T_A}}$$

Kirchhoff rules extended to ΔS

- Now we can calculate both H and S from C_p at T_2

The same formula is used to measure entropy in a calorimeter

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_P dT}{T} \approx C_P \ln\left(\frac{T_2}{T_1}\right)$$

- $\Delta H \approx C_P(T_2 - T_1)$ (Kirchhoff)

For $\Delta T << T_1$

$$S(T_2) \approx S(T_1) + C_P \ln\left(\frac{T_2}{T_1}\right)$$

$$S(T_2) \approx S(T_1) + C_P\left(\frac{T_2 - T_1}{T_1}\right)$$

$$H(T_2) \approx H(T_1) + C_P(T_2 - T_1)$$

Entropy in Statistical Thermodynamics

- ***Entropy* is a measure of *number of states***

- $S = -k \sum p_i \ln p_i$, where:
  - p_i is the probability of the microstate i
  - k (or k_B) is the Boltzmann constant
- If the microstates are equi-probable:

$$S = k \ln W$$

where W is the number of microstates for the *entire system* (*distinguishable ways* the system can be put together with given U and V), $W_{mole} = n_1^{Na}$

- $S_{mole} = S_m = R \ln (n_1)$ if ***n*** is the number of microstates for one molecule.

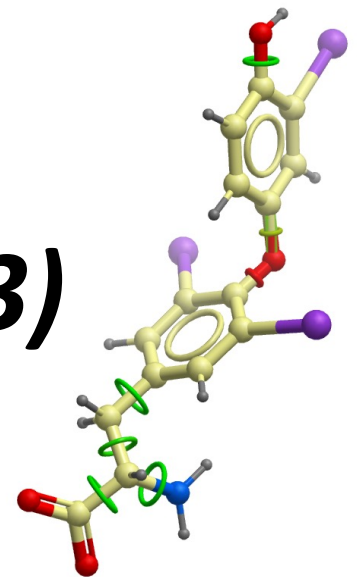- $\Delta S_{m\ a \to b} = S_b - S_a = R \ln (n_b/n_a)$

Entropy Changes: Examples

- Configurational Entropy of one molecule in a transition from one conformation to all possible ones.

- Example: the number of states **W** in one molecule, with n_b rotatable bonds with 3 equi-probable states, n is # states in 1 molecule

$$S_m = R\ ln\ (n)$$

$$n = 3^{n_b}$$

$$\Delta s_{from\ 1\ to\ n\ states} = R \times n_b \times ln(3)$$

Entropy is **Additive** : $S_{AB} = S_A + S_B$

- Entropy of two parts, A and B

$S_A = k \ln n_A$, $S_B = k \ln n_B$,

- Entropy of *both* parts , A + B:

    The number of states: $\boldsymbol{n_{AB} = n_A \, n_B}$

    $S_{AB} = k \ln(n_A \, n_B) = k \ln n_A + k \ln n_B = S_A + S_B$

    Entropy is ADDITIVE, since $\ln XY = \ln X + \ln Y$

- For the Avogadro number of molecules with n_1 states: $S_{mole} = N_A \, k \ln n_1 = R \ln n_1$

Standard **Entropies** of Formation

Compound	s_m^o /J K^{-1}mol^{-1}
Diatomic Gases	
H_2	130.7
D_2	145.0
HCl	186.9
HBr	198.7
HI	206.6
N_2	191.6
O_2	205.1
F_2	202.8
Cl_2	223.1
Br_2	245.5
I_2	260.7	Solid: 116
CO	197.7
Triatomic Gases	
H_2O	188.8
NO_2	240.1
H_2S	205.8
CO_2	213.7
SO_2	248.2

Compound	s_m^o /J K^{-1}mol^{-1}
Solids	
C (diamond)	2.377
C (graphite)	5.74
Liquids	
Hg	76.0
Br_2	152.2
H_2O	69.9
H_2O_2	109.6
CH_3OH	126.8
C_2H_5OH	160.7
C_6H_6	172.8
BCl_3	206.3
Monatomic Gases	
He	126.0
Ne	146.2
Ar	154.8
Kr	164.0
Xe	169.6

$$\Delta S_m = S_2 - S_1 = R\ \ln(n_2/n_1)$$

- The number of vibration *quantum* microstates depends on the atom masses
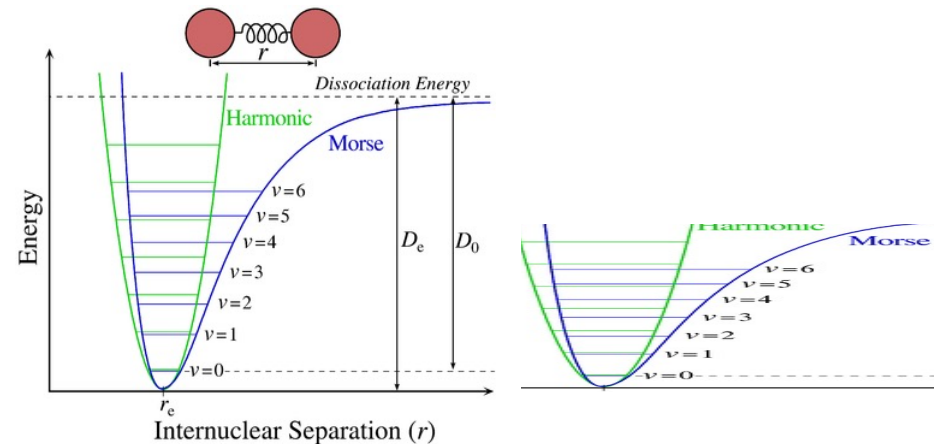
$$\Delta S°_{rxn} = S_f°_{products} - S_f°_{reactants}$$

Entropy Summary: $S_{molar} = R \ln n$

- $S = k \ln N$ for any number of molecules, N is the total number of combinations of micro-states for all molecules.

- $N = n^{N_A}$ for 1 mole (N_A is *Avogadro number*) of molecules, n is the number of states per MOLECULE

- S for one mole: $S_m = k \ln N = k N_A \ln(n) = R \ln n$

- S for m moles is $m S_m$ (entropy is additive)

- $\Delta S_{m\ 1 \to 2} = R \ln (n_2/n_1)$

Estimating $\ln(1+x)$ and more

- In many problems you need to estimate expressions looking like

  $\ln(300K/280.) \approx \ln(1.07)$ or 1/1.2, etc.

- To evaluate them use a simple technique based on the *Taylor* expansion:

$$f(a+x) = f_a + xf_a' + \frac{x^2}{2}f_a'' + .. + \frac{x^n}{n!}f_a^{(n)}$$

$$\ln(1+x) \approx x$$

$$e^x \approx 1+x$$

$$(1+x)^n \approx 1+nx$$

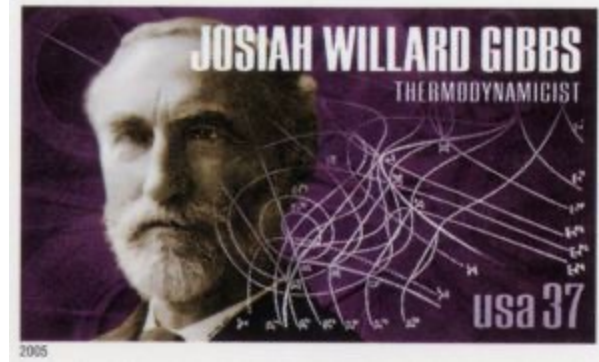$$Examples: n = -1, \frac{1}{2}, 2$$

$$\frac{1}{1+x} \approx 1-x$$

$$\sqrt{(1+x)} \approx 1 + \frac{1}{2}x$$

$$(1+x)^2 \approx 1+2x$$

$$E.g. \ln(1.07) \approx 0.7$$

Gibbs Free Energy

JOSIAH WILLARD GIBBS
THERMODYNAMICIST
usa 37
2005

1839-1903, American theoretical physicist

What function defines the direction of processes at constant temperature and pressure (biology) ?

$$G = H - TS$$

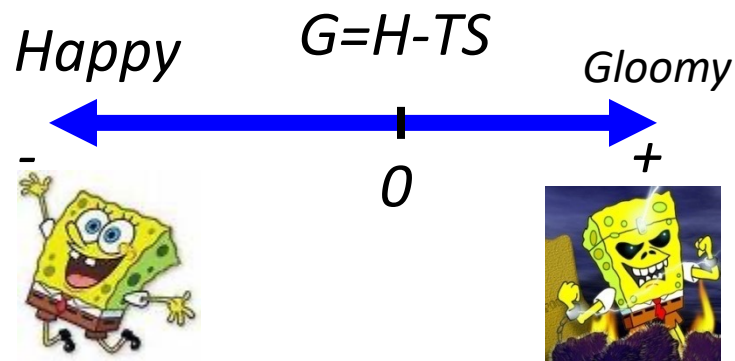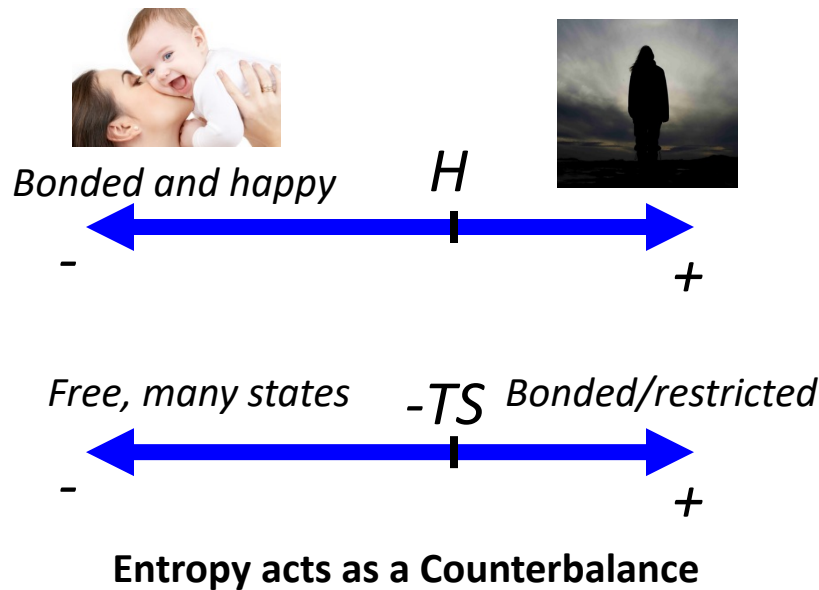$\Delta G = \Delta H - T\Delta S$ (Free Energy Change in a Transition)

- **G** defines the direction of transformations and reactions
- Chemical reactions are **spontaneous** in the direction of decreasing **G**, i.e. $dG_{T,P} \leq 0$
- In chemical or phase equilibrium $G_1 = G_2$ or $\Delta G = 0$
- **G** defines maximal useful (non-expansion) work that can be extracted from the system

Minimize G by bonding and having more states

- Enthalpy (**H**) push to more bonds is counteracted by Entropy (**S**) push for more states.

- *Reducing* **H** by forming more strong bonds

- Entropy (**S**) is freedom, ln(**S**tates), ability to have many options, personal **S**pace. You want to *increase* S (thus reducing –TS). Freedom contribution, **-TS**, to G increases with temperature.

- **Temperature** is the relative importance of freedom and Entropy in total balance

$$G = H - TS$$

- Goal: Minimize G by reducing H and increasing S.

- *G,H,TS* measured in the J, kJ, or cal/kcal

Bonded and happy H

− +

Free, many states -TS *Bonded/restricted*

− +

Entropy acts as a Counterbalance

Happy G=H-TS *Gloomy*

− 0 +

Review

- State functions (variables)
- 1st Law, work $\Delta U = q - w$
- Enthalpy $H = U + PV$
- Calorimetry
- Heat capacity, $\mathbf{C} \equiv q / \Delta \mathrm{T}$
- C_v and C_p $\qquad C_p \equiv \left(\dfrac{\partial H}{\partial T} \right)_P$
- Molar C, specific heat $\qquad C_v \equiv \left(\dfrac{\partial U}{\partial T} \right)_V$
- Transitions, standard states

Gibbs Free Energy (G)

$$G = H - TS$$

$$G_1 = G_2$$

$$G \rightarrow minimum$$

- Hess rules for H
- Entropy

$$dS = \frac{dq_{rev}}{T} \quad \text{or} \quad \Delta S = \int_A^B \frac{dq_{rev}}{T}$$

- Entropy from C_p at T_2

$$H(T_2) \approx H(T_1) + C_P(T_2 - T_1)$$

$$S(T_2) \approx S(T_1) + C_P \ln\left(\frac{T_2}{T_1} \right)$$

- Entropy of gas from (p_1, v_1) to (p_2, v_2):

$$\Delta S_T = nR \ln(v_1/v_2)$$
$$\Delta S_T = -nR \ln(p_1/p_2)$$

- $S_{mole} = k_B \ln (N_{total})$

$$= R \ln (n_{states\_of\_one\_molecule})$$

$$\Delta S = nR \ln(n_1/n_2)$$
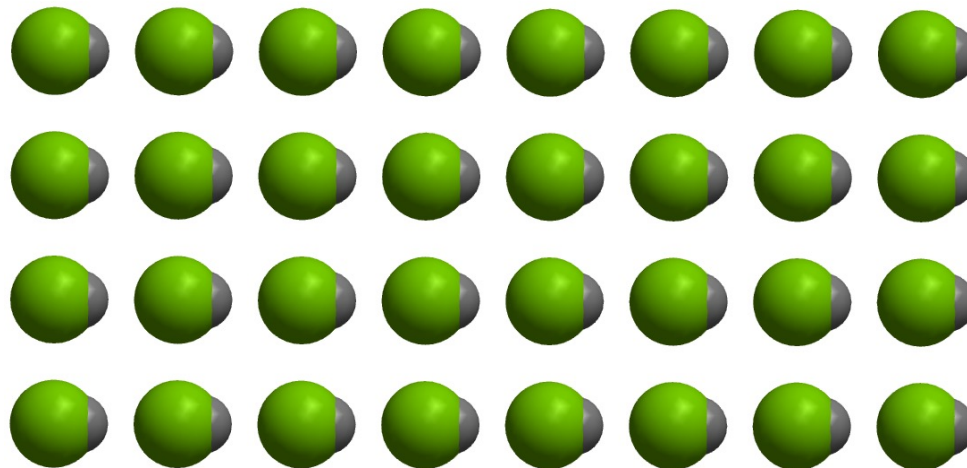
Example: Entropy and Growing Crystals - I

HCl – hydrogen chloride

- Low entropy – perfect crystals

- Once the 1st molecule is in place, there is only *one* way to put the crystal together (W total number of states):

$$W = 1$$

- At $T = 0$,

$$S = k \ln W = k \ln 1 = \mathbf{0}$$

Example: Entropy and Growing Crystals - II

CO – carbon oxide

- Higher entropy – imperfect (rotationally disordered) crystals

- Once the 1st molecule is in place, there are *two* ways to position the 2nd molecule, for each of these, *two* ways to position the 3rd molecule etc:

    Number of states for N molecules $W = 2^N$

- At $T = 0$,

    $$S = k \ln W = k \ln 2^N = Nk \ln 2$$

- For a *mole* of CO,

    $$S = (N_A k) \ln 2 = R \ln 2$$

    (R – gas constant)