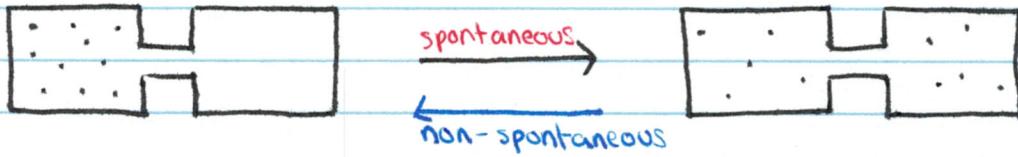


Spontaneity

- spontaneous process = physical or chemical process (change) that occurs by itself without outside interventions (ex: work done by external force is not spontaneous)
- * Implies that it is energetically favourable for the process to occur in a specific direction
Note: Does not mean fast
 - Can be fast/slow, endo / exothermic
- * Spontaneous direction is always towards greater dispersal of matter / energy



Reversible / Irreversible processes

- * If a process is spontaneous in one direction, it must be non-spontaneous in the opposite direction (see example above)
- Any spontaneous process is **irreversible** because there is a net release of free energy when it proceeds in that direction (proceeds in one direction)
ex: rusting = $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$
- A **reversible** process will proceed back and forth between the two end conditions (at equilibrium)
ex: melting ice at 0°C = $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ (coexistence)

Entropy : measure of dispersal (disorder)

→ The driving force for a spontaneous process is an increase in the entropy of the universe.

Think: Your room. As time passes, your room spontaneously becomes disordered (entropy). However, to go back to a clean / ordered room, it requires energy input.

Entropy (S) = a thermodynamic function that describes the number of arrangements (positions / energy levels) that are available to a system existing at a given state : temp.
[J/K]

→ Entropy is closely associated with probability. The more ways a particular state can be achieved, the greater the likelihood of finding that state.

$$S = K \ln W$$

W = number of microstates

- entropy can be calculated

Microstates

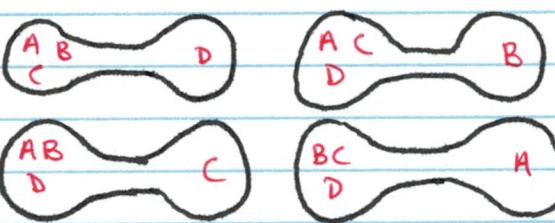
- microstate of system = each configuration that gives a particular arrangement of the positions and kinetic energies of the molecules in a specific thermodynamic state
- Nature spontaneously proceeds towards the states that have the highest probabilities of existing.

Possible Arrangements of 4 molecules in 2-bulb

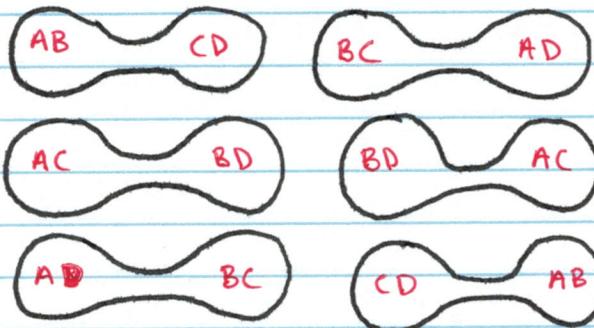
①



②

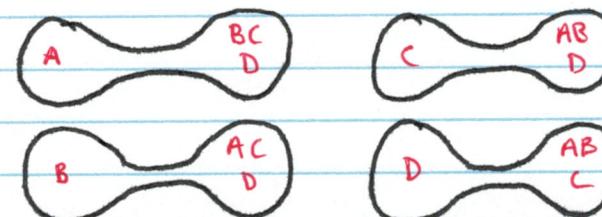


③



Arrangements most likely to occur have highest number of microstates

④



⑤



Entropy of Pure Substances

Third Law of Thermodynamics =
A perfect crystal at 0 K (no kinetic energy)
has zero entropy $\Rightarrow S = 0$

(i) $T = 0 \text{ K} \Rightarrow S = 0$
Absolutely Regular



(ii) $T > 0 \text{ K} \Rightarrow S > 0$
Disorder increases



\rightarrow We can assign absolute entropy values to compounds (contrary to enthalpy)

Standard Entropy Values (S°) [J/mol.K]

- \rightarrow molar entropy values of substances in their standard states
- $\rightarrow S^\circ$ = increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm

Phase Changes

- \rightarrow Entropy is a measure of molecular disorder
- \rightarrow Solids are more ordered than liquids or gases, so they have lower entropy

$$S_{(\text{solid})} < S_{(\text{liquid})} \ll S_{(\text{gas})}$$

$$\text{H}_2\text{O}: S^\circ_{(s)} = 48 \frac{\text{J}}{\text{K.mol}} < S^\circ_{(l)} = 70 \frac{\text{J}}{\text{K.mol}} < S^\circ_{(g)} = 189 \frac{\text{J}}{\text{K.mol}}$$

better organised better organised

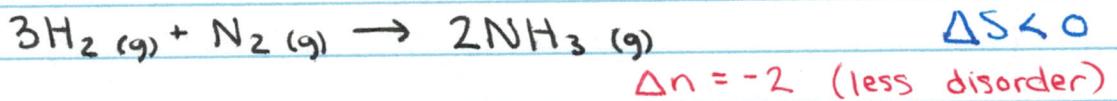
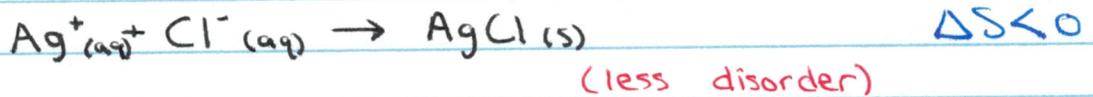
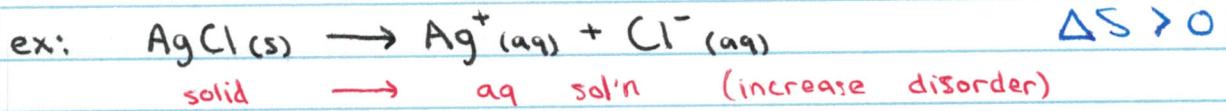
Predicting ΔS_{sys}

→ Entropy is a state function (path independant)

$$\boxed{\Delta S_{sys} = S_f - S_i}$$

* Expect increase in entropy (increase disorder) if:

- (i) Gases formed from liquids / solids
- (ii) Liquids or solns formed from solids
- (iii) Number of gas molecules increases ($\Delta n > 0$)



Calculate ΔS_{rxn}

$$\boxed{\Delta S^\circ_{rxn} = \underbrace{\sum n_p S^\circ_{products}}_{\text{Product}} - \underbrace{\sum n_r S^\circ_{reactants}}_{\text{Reactant}}}$$

ex: calculate ΔS° for $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$

$$S^\circ(\text{NH}_3) = 192.5 \text{ J/K mol}$$

$$S^\circ(\text{N}_2) = 191.5 \text{ J/K mol}$$

$$S^\circ(\text{H}_2) = 130.6 \text{ J/K mol}$$

$$\begin{aligned} \Delta S_{rxn} &= [2\text{mol NH}_3 \times 192.5] - [(1\text{mol N}_2 \times 191.5) + (3\text{mol H}_2 \times 130.6)] \\ &= -198.3 \frac{\text{J}}{\text{K}} \end{aligned}$$

Second Law of Thermodynamics

- Energy is conserved (1st law)
- Entropy is not: entropy of the universe is increasing.

Second Law = any spontaneous process, there is an increase of entropy of the universe

For process to be spontaneous: $\Delta S_{\text{universe}} > 0$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Predict spontaneity:

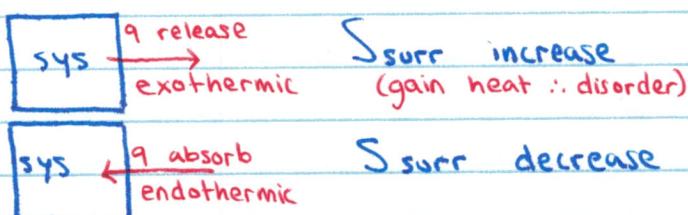
- $\Delta S_{\text{uni}} > 0$ (pos.) \Rightarrow process is spontaneous in forward direction
- $\Delta S_{\text{uni}} < 0$ (neg.) \Rightarrow process is non-spontaneous, spontaneous in reverse direction
- $\Delta S_{\text{uni}} = 0$ \Rightarrow process at equilibrium

ΔS_{surr} : entropy change of surroundings

$$\Delta S_{\text{surr}} = - \frac{\Delta H_{\text{sys}}}{T}$$

ΔH [J]
 T [K]

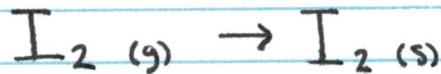
at constant T and P



ΔS_{surr} inversely proportional to T :

→ if temp is already high, heat doesn't make big difference, give 100\$ to millionaire vs homeless person.

ex: determine ΔS_{surr} of I_2 deposition



$$\Delta H = -62 \text{ kJ/mol}$$

$$T = 25^\circ\text{C}$$

predict ΔS of sys and surr

① $g \rightarrow s \therefore \text{less disorder} \therefore \Delta S_{\text{sys}} < 0$

② exothermic



$$\therefore \Delta S_{\text{surr}} > 0$$

$$\text{Calculate: } \Delta S_{\text{surr}} = -\frac{\Delta H}{T} = -\left(\frac{-62 \times 10^3 \text{ J}}{298 \text{ K}}\right) = 208 \frac{\text{J}}{\text{K}}$$

ex: determine if process is spontaneous



at 298 K

$$S^\circ(NaCl(aq)) = 115.5 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$S^\circ(NaCl(s)) = 72.11 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta H_f^\circ(NaCl(aq)) = -407.27 \text{ kJ/mol}$$

$$\Delta H_f^\circ(NaCl(s)) = -411.12 \text{ kJ/mol}$$

$$\Delta H_{\text{sys}}^\circ = (-407.27 \times 1 \text{ mol } NaCl(aq)) - (-411.12 \times 1 \text{ mol } NaCl(s)) = \\ = 3.85 \text{ kJ}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}^\circ}{T} = -\left(\frac{3.85 \times 10^3 \text{ J}}{298 \text{ K}}\right) = -12.9 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{sys}} = \left(1 \text{ mol } NaCl(aq) \times 115.5 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) - \left(1 \text{ mol } NaCl(s) \times 72.11 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) \\ = 43.4 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{universe}} = \underbrace{(43.4 \frac{\text{J}}{\text{K}})}_{\text{sys}} + \underbrace{(-12.9 \frac{\text{J}}{\text{K}})}_{\text{surr}} = 30.5 \frac{\text{J}}{\text{K}}$$

$\Delta S_{\text{uni}} > 0 \therefore \text{spontaneous}$

Free Energy (G)

$$G = H - TS$$

$$\Delta G^\circ_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

ΔG [J]

ΔH [J]

T [K]

ΔS [J/K]

Derive formula:

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \left(-\frac{\Delta H_{\text{sys}}}{T} \right)$$

multiply by $-T$

$$\underbrace{-T\Delta S_{\text{uni}}}_{= -T\Delta S_{\text{sys}} + \frac{-T \cdot -\Delta H_{\text{sys}}}{T}} = -T\Delta S_{\text{sys}} + \frac{-T \cdot -\Delta H_{\text{sys}}}{T}$$

By def:

$$\Delta G_{\text{sys}} = -T\Delta S_{\text{uni}}$$

$$\Delta G_{\text{sys}} = -T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}$$

Predict Spontaneity at constant T and P :

- $\Delta G < 0 \Rightarrow$ spontaneous forward
- $\Delta G > 0 \Rightarrow$ non-spontaneous forward, spontaneous in reverse direction
- $\Delta G = 0 \Rightarrow$ equilibrium

Note: opposite of
 ΔS_{uni} b/c $\Delta G = -T\Delta S_{\text{uni}}$



ex: melting water



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

$$T = -10^\circ\text{C} \quad \Delta G \approx 2.2 \times 10^2 \text{ J} \Rightarrow \Delta G > 0 \quad \therefore \text{non-spontaneous} \\ (\text{reverse spontaneous})$$

$$T = 0^\circ\text{C} \quad \Delta G \approx 0 \quad \Rightarrow \Delta G = 0 \quad \therefore \text{equilibrium}$$

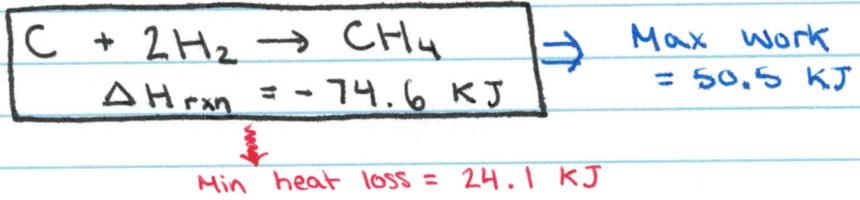
$$T = 10^\circ\text{C} \quad \Delta G \approx -2.2 \times 10^2 \text{ J} \Rightarrow \Delta G < 0 \quad \therefore \text{spontaneous}$$

Free Energy and Useful Work

- ΔG_{rxn} = maximum amount of energy,
(neg) available (free) to do work.
- ΔG_{rxn} = minimum amount of energy
(pos) required for reaction to occur.

* At constant T and P, $\Delta G = W_{useful}$

ex:



EFFECT OF TEMPERATURE ON SPONTANEITY

ΔH_{sys}	ΔS_{sys}	$\Delta G = \Delta H - T\Delta S$	Spontaneous?
-	+	-	Spontaneous (always)
+	-	+	Non-Spontaneous (always)
Depend on T.	-	-	+ or -
	+	+	+ or -

ΔH and ΔS pos $\Rightarrow T > T_{equil} \rightarrow$ spontaneous
 ΔH and ΔS neg $\Rightarrow T < T_{equil} \rightarrow$ spontaneous

T_{equil} = temperature at which non-spontaneous becomes spontaneous
= temperature where $\Delta G_i = 0$ (equil)
= boiling point, melting point, etc.



$$\Delta H = 95.7 \text{ kJ}$$
$$\Delta S = 142.2 \text{ J/K}$$

both pos.

① Calculate ΔG° at 298 K

$$\Delta G^\circ = \Delta H - T\Delta S$$

$$= 95.7 \times 10^3 \text{ J} - 298 \text{ K} \times 142.2 \text{ J/K}$$

$$= 53.3 \times 10^3 \text{ J}$$

$\therefore \Delta G^\circ > 0 \therefore \text{non-spontaneous}$

② Calculate temp for equilibrium

$$\text{Set } \Delta G^\circ = 0$$

$$0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{95.7 \times 10^3 \text{ J}}{142.2 \text{ J/K}} = 673 \text{ K}$$

$\therefore \text{At } 673 \text{ K} \Rightarrow \text{equilibrium}$

At higher T \Rightarrow spontaneous

At lower T \Rightarrow non-spontaneous (ex: 298 K)

ex: Phase changes occur at equilibrium

What is normal boiling point of bromine?

$$\Delta H_{\text{vap}} = 31.0 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}} = 93.0 \text{ J/K.mol}$$



$$\text{Set } \Delta G^\circ = 0$$

$$T = \frac{\Delta H}{\Delta S} = \frac{31 \times 10^3 \text{ J/mol}}{93 \text{ J/K.mol}} = 333 \text{ K}$$

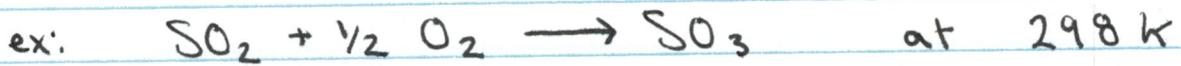
$\therefore \text{At } 333 \text{ K} \Rightarrow \text{boiling point}$

At higher T \Rightarrow forward spontaneous

At lower T \Rightarrow forward non-spontaneous

Calculating Free Energy for rxn (ΔG°_{rxn})

① Calculate ΔH°_{rxn} and ΔS°_{rxn}
 $\hookrightarrow \Delta G$



ΔH_f° (kJ/mol)	-296.8	0	-395.7
ΔS° (J/K·mol)	248.2	205.2	256.8

$$\Delta H = [1\text{ mol } SO_3 \times (-395.7)] - [1\text{ mol } SO_2 \times (-296.8)] = -98.9 \text{ kJ}$$

$$\Delta S = [1\text{ mol} \times 256.8] - [1\text{ mol} \times 248.2 + \frac{1}{2}\text{ mol} \times 205.2] = -94 \frac{\text{J}}{\text{K}}$$

$$\begin{aligned} \therefore \Delta G &= \Delta H - T \Delta S \\ &= (-98.9 \times 10^3 \text{ J}) - 298 \text{ K}(-94 \text{ J/K}) \\ &= -7.09 \times 10^4 \text{ J} \quad \Delta G < 0 \therefore \text{spontaneous} \end{aligned}$$

② Calculate from ΔG_f° values

$$\boxed{\Delta G_{rxn}^\circ = \sum n_p \Delta G_f^\circ (\text{products}) - \sum n_r \Delta G_f^\circ (\text{reactants})}$$

Note: ΔG_f° of pure elements in standard states = 0



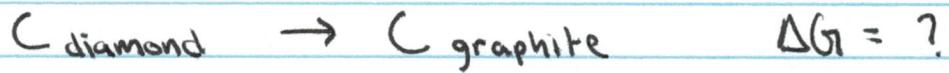
ΔG_f° (kJ/mol)	-50.8	0	-228.6	-394.4
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$$\begin{aligned} \Delta G_{rxn}^\circ &= [2\text{ mol} \times (-228.6) + 1\text{ mol} \times (-394.4)] - [1\text{ mol} \times (-50.8)] \\ &= -801 \text{ kJ} \text{ at 298 K} \end{aligned}$$

$\therefore \Delta G < 0 \therefore \text{spontaneous}$

③ Calculate using Hess's Law

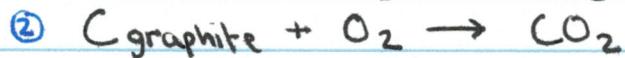
ex: Calculate ΔG°_{rxn} (at 298 K) of



given:



$$\Delta G = -397 \text{ KJ}$$



$$\Delta G = -394 \text{ KJ}$$



$$\Delta G = -397 \text{ KJ}$$



$$\Delta G = +394 \text{ KJ}$$



$$\Delta G = -3 \text{ KJ}$$

$\Delta G < 0 \therefore \text{spontaneous}$