Topic 9.1: Introduction to Entropy

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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Entropy Measures Dispersal

The definition. Entropy, S, measures how dispersed the matter and energy of a system are: a gas filling a room is highly dispersed, particles in a crystal lattice are not.

Microstates. Each arrangement of particles and energy that a system can adopt is a microstate. A dispersed system can be arranged in vastly more ways than a confined one, so more microstates mean higher entropy.

A state function. Entropy depends only on the state of the system, not the path taken: what matters is the change between the two states.

$\Delta S = S(\text{final}) - S(\text{initial})$

The Phase Order Comes First

Solid, then liquid, then gas. For the same substance at the same conditions, entropy always runs in one order. Particles in a solid hold fixed positions, in a liquid they slide past each other, and in a gas they move freely through the whole container.

$S(\text{solid}) < S(\text{liquid}) < S(\text{gas})$

Signs follow the direction. Moving up the order gives $\Delta S > 0$: melting, vaporization, sublimation. Moving down gives $\Delta S < 0$: freezing, condensation, deposition.

Not all upward steps are equal. Vaporization produces the largest entropy jump of the common phase changes: melting only loosens a lattice, vaporization separates the particles completely.

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Count Gas Moles for Reactions

The rule. Compare the moles of gas on each side of the balanced equation. More gas on the product side means $\Delta S > 0$. Fewer means $\Delta S < 0$. The same number on both sides means ΔS is close to zero, because the dispersal of the gas particles barely changes.

Why gas dominates the count. A mole of gas offers far more microstates than a mole of solid or liquid, so gas mole changes swamp every other effect.

Three patterns to recognize on sight. A solid releasing a gas has zero moles of gas become one, so $\Delta S > 0$.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

A gas consumed into a liquid has three moles become none, so $\Delta S < 0$.

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

A gas for gas swap has two moles on each side, so ΔS is small.

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

Dissolving, Mixing and Spreading Out

Dissolving a solid usually raises entropy. When NaCl(s) dissolves, the ions leave a rigid lattice and move freely through the water, so $\Delta S > 0$.

The gas exception. Dissolving a gas in a liquid runs the other way, because the gas particles lose the run of their container and are confined in the liquid.

$CO_2(g) \rightarrow CO_2(aq)$

That change has $\Delta S < 0$.

Mixing and expanding are always positive. Mix two different gases and each spreads into the full volume: $\Delta S > 0$ with no reaction at all. Let a gas expand into an evacuated chamber and the same particles occupy more volume: $\Delta S > 0$ again. Compress the gas instead and its entropy falls.

Temperature, Amount and Molecular Size

Heat raises entropy. Warming a sample spreads its energy over more microstates, so entropy rises with temperature, and cooling any sample lowers its entropy.

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Amount and volume count too. Entropy is extensive: at the same temperature and pressure, 1 mol of a gas has more entropy than 0.5 mol of it. A mole of gas at lower pressure occupies more volume and is more dispersed, so it too has the greater entropy.

Bigger molecules carry more entropy. At the same phase and conditions, a larger, more complex substance has the higher standard molar entropy: more atoms and more bonds mean more ways to distribute energy.

The zero point. A perfect crystal at absolute zero has exactly one microstate, so its entropy is zero: the third law anchor for absolute entropies.

The Universe Keeps the Score

The second law. For any spontaneous process, the entropy of the universe increases. The universe means the system plus everything around it, and the law judges the total, never the system alone.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$

A falling system entropy proves nothing. Freezing, condensation and ammonia synthesis all lower the entropy of the system, yet each can be spontaneous. What rescues them is the surroundings term: heat released raises $\Delta S_{surroundings}$ by more than the system lost.

The two anchor cases. Water freezes spontaneously at −10 °C: ΔS_{system} is negative, but the heat released raises the entropy of the cold surroundings by a larger positive amount. Dissolving NH_4NO_3 is endothermic yet spontaneous: $\Delta S_{surroundings}$ falls as heat is absorbed, but the dispersing ions raise ΔS_{system} by more.

Worked Examples

> **Example 1: Four reactions, four sign predictions. Count gas moles, reactants first, products second. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$: 4 become 2, $\Delta S < 0$, the most negative of this set. $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$: 3 become 2, $\Delta S < 0$ by a smaller margin. $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$: 2 become 2, ΔS close to zero. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$: 0 become 1, $\Delta S > 0$. Most negative to most positive: ammonia synthesis, SO_2 oxidation, HCl formation, carbonate decomposition.**

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Example 3: Which sample has the greatest entropy. Compare 1 mol of Ne(g) at 600 K and 1 atm with 1 mol at 300 K and 2 atm and 0.5 mol at 600 K and 1 atm. The 1 mol sample at 600 K and 1 atm wins: it is hotter than the 300 K sample, it holds a full mole against the half mole sample, and its lower pressure gives it more volume per mole.

Example 4: A gas compressed by a piston. Compressing a gas isothermally confines its particles to less volume, so ΔS(system) is negative. The work done on the gas leaves as heat, and that heat disperses energy in the surroundings, so ΔS(surroundings) is positive. The system term alone cannot judge the process; only the sum of the two terms can.

Example 2: The universe test with numbers. A process has ΔS(system) = −50 J/K. Spontaneity requires ΔS(universe) > 0, so ΔS(surroundings) must exceed +50 J/K. Exactly +50 J/K gives a total of zero: equilibrium, not spontaneous. A surroundings gain of +60 J/K gives ΔS(universe) = +10 J/K, and the process runs.

Traps That Cost Marks in Topic 9.1

"Spontaneous means the system gets messier." No: spontaneous means the universe gets messier. A system can order itself, as freezing water does, provided the surroundings gain more entropy than the system loses.

"ΔS is exactly zero when gas moles are unchanged." Close to zero, not zero: the reaction below barely changes dispersal, but barely is not exactly.

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

"Dissolving always increases entropy." Dissolving a solid usually does. Dissolving a gas decreases it, because the gas is captured into a far smaller volume.

"A more complex product guarantees ΔS > 0." Complexity raises standard molar entropy when comparing substances, but a reaction's ΔS follows the change in the system, and the gas mole count dominates. Two moles of gas forming two moles of a more complex gas still gives ΔS close to zero.

Reading the phase direction backwards. Sublimation (solid to gas) is positive, deposition (gas to solid) negative. Name both phases before assigning the sign.

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Comparing samples on one variable only. Entropy grows with amount as well as temperature, so a hotter half mole can lose to a cooler full mole. Check all the variables before ranking.

Key Relationships to Remember

- Entropy S measures the dispersal of matter and energy; more microstates mean higher entropy
- S(solid) < S(liquid) < S(gas); upward phase changes have $\Delta S > 0$, downward ones $\Delta S < 0$, and vaporization gives the largest increase
- Reaction ΔS sign: count gas moles; more gas produced means $\Delta S > 0$, less means $\Delta S < 0$, unchanged means ΔS close to zero
- Dissolving a solid usually has $\Delta S > 0$; dissolving a gas in a liquid has $\Delta S < 0$
- Mixing gases, and a gas expanding into more volume, have $\Delta S > 0$; compression has $\Delta S < 0$
- Entropy rises with temperature and amount, and is higher for larger, more complex molecules in the same phase
- Second law: $\Delta S(\text{universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) > 0$ for a spontaneous process; zero means equilibrium
- A perfect crystal at 0 K has S = 0 (third law)

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