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# Topic 9.1: Introduction to Entropy

Worksheet · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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## How to Use This Worksheet

Work in order. Section A checks the ideas: the dispersal definition, the phase order, the third law and the second law. Section B practices the sign rules: counting gas moles, dissolving, mixing and expanding, comparing samples, and an endothermic process that runs anyway. Section C is exam style: universe arithmetic with real numbers, freezing analyzed term by term, and a ranking problem with a claim to judge.

Reference facts: no data tables are needed anywhere on this sheet. Key values: the phase order is solid < liquid < gas, and the universe test is given below. Every answer is a sign, a ranking, or a short piece of arithmetic on ΔS values given in the question. Temperatures are in kelvin for samples and in °C where a process is described, exactly as the exam mixes them.

One working habit ties the sheet together: run the checks in order. Phase first (solid < liquid < gas), then gas moles in the balanced equation (more gas produced means $\Delta S > 0$, fewer means $\Delta S < 0$, unchanged means close to zero), then dispersal processes (dissolving, mixing, expanding), and only then the universe test, which alone decides spontaneity. The system term by itself decides nothing.

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

The answer key gives the full reasoning for every part. Attempt every question before looking at it.

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## Section A: Recall and Concepts

**A1.** (a) Define entropy in terms of dispersal. (b) Explain, using microstates, why a gas has a far higher entropy than the same substance as a solid. (c) Entropy is a state function: state what that means for the value of ΔS between two states.

**A2.** (a) Rank 1 mol each of ice, liquid water and steam by entropy, greatest first. (b) Give the sign of ΔS for each of these changes to water: melting, condensation, sublimation, deposition. (c) Of melting and vaporization, state which produces the larger entropy increase and why.

**A3.** (a) State the third law of thermodynamics. (b) Explain why a perfect crystal at 0 K has exactly one microstate. (c) State what the third law makes possible that the first two laws do not.

**A4.** (a) State the second law of thermodynamics. (b) Write the equation connecting ΔS(universe), ΔS(system) and ΔS(surroundings). (c) State what ΔS(universe) = 0 and ΔS(universe) < 0 each tell you about a process.

**A5.** Judge each claim, giving a reason. (a) "Entropy is a measure of the heat a reaction releases." (b) "If ΔS(system) is negative, the process cannot be spontaneous." (c) "The entropy change for $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$ is exactly zero." (d) "Dissolving a substance in water always increases the entropy of the system."

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## Section B: Core Practice

**B1.** For each reaction, count the moles of gas on each side and predict the sign of ΔS, stating Δn(gas) each time. (a) $2\ H_2O_2(l) \rightarrow 2\ H_2O(l) + O_2(g)$ (b) $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ (c) $C(s) + O_2(g) \rightarrow CO_2(g)$ (d) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

**B2.** Rank the four reactions of B1 from the most negative ΔS to the most positive ΔS. For the two negative cases, state what decides which is more negative. For the case closest to zero, state why it is not exactly zero.

**B3.** (a) State the sign of ΔS when NaCl(s) dissolves in water, and explain it at the particle level. (b) State the sign of ΔS when $CO_2(g)$ dissolves in water to give $CO_2(aq)$, and explain it. (c) Both processes are "dissolving": state the feature that makes their signs opposite.

**B4.** Predict the sign of the entropy change of the system for each change, with a one-line reason. (a) Two different ideal gases are mixed in a rigid container at constant temperature. (b) A gas expands into an evacuated chamber at constant temperature. (c) A gas is compressed isothermally by a piston. (d) A cold solid is warmed from 200 K to 300 K. (e) A gas cools and condenses into a liquid.

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**B5.** In each pair, state which sample has the greater entropy, and name the variable that decides it. (a) 1 mol of Ne(g) at 300 K and 1 atm, or 1 mol of Ne(g) at 300 K and 2 atm. (b) 0.5 mol of Ne(g) at 600 K and 1 atm, or 1 mol of Ne(g) at 600 K and 1 atm. (c) 1 mol of Ne(g) at 300 K and 1 atm, or 1 mol of Ne(g) at 600 K and 1 atm. (d) 1 mol of Ne(g) at 600 K and 1 atm, or 0.5 mol of Ne(g) at 600 K and 2 atm.

**B6.** Solid $NH_4NO_3$ dissolves in water spontaneously even though the process is endothermic. (a) State the sign of ΔS(system) and give the particle-level reason. (b) The process absorbs heat from the surroundings: state the sign of ΔS(surroundings). (c) Using the second law, explain how the process can still be spontaneous. (d) State the sign of ΔS(universe).

## Section C: Exam Style

**C1.** A process has ΔS(system) = −80 J/K. (a) State the condition on ΔS(surroundings) for the process to be spontaneous. (b) The surroundings entropy change is measured at exactly +80 J/K: state ΔS(universe) and what this situation is called. (c) On a colder day the surroundings entropy change for the same process is +95 J/K: calculate ΔS(universe) and state whether the process is spontaneous. (d) A second process has ΔS(system) = +45 J/K and ΔS(surroundings) = −60 J/K: calculate ΔS(universe), state whether it runs as written, and state what happens instead.

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**C2.** Water freezes spontaneously at −10 °C, even though freezing orders the water. (a) State the sign of ΔS(system) for the freezing water. (b) Freezing releases heat to the surroundings: state the sign of ΔS(surroundings) and explain why released heat raises the entropy of the surroundings. (c) State the sign of ΔS(universe), and the law that requires it. (d) At −10 °C the reverse process, melting, does not happen on its own: state what the second law says about the sign of ΔS(universe) for melting at this temperature, without calculating anything.

**C3.** (a) Predict the sign of ΔS for each reaction: (i) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (ii) $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ (iii) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$ (iv) $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$. (b) State which reaction has the most negative ΔS, and what decides it. (c) A student claims reaction (iv) must have ΔS = 0 "because $SO_3$ is a more complex molecule, and complexity cancels the mole change." Judge the claim. (d) State which reaction has ΔS closest to zero, and explain why "closest" is the right word rather than "equal".

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## Answer Key

**A1.** (a) Entropy is a measure of how dispersed the matter and energy of a system are: the more spread out they are, the higher the entropy. (b) Particles in a solid hold fixed positions in a lattice, allowing very few arrangements. Particles in a gas move freely through the whole volume, so the particles and their energy can be arranged in vastly more ways (microstates), and more microstates mean higher entropy. (c) $\Delta S$ depends only on the initial and final states, $\Delta S = S(\text{final}) - S(\text{initial})$. The path taken between them, fast or slow, one step or many, does not change the value.

**A2.** (a) Steam > liquid water > ice. Freedom of the particles rises from solid to liquid to gas, so entropy follows the same order. (b) Melting: positive, the lattice breaks up. Condensation: negative, gas particles are packed into a liquid. Sublimation: positive, a solid becomes a gas directly. Deposition: negative, a gas becomes a solid directly. (c) Vaporization. Melting only loosens the particles from fixed positions, while vaporization separates them completely into the gas phase, a far larger gain in dispersal.

**A3.** (a) The entropy of a perfect crystalline solid at absolute zero (0 K) is zero. (b) At 0 K the particles have no thermal motion and sit in a single perfect arrangement, so exactly one microstate exists, and one arrangement carries no dispersal at all. (c) It provides a fixed zero point, which makes absolute entropy values for substances meaningful rather than only differences between states.

**A4.** (a) For any spontaneous process, the entropy of the universe increases. (b) $\Delta S(\text{universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$. (c) $\Delta S(\text{universe}) = 0$ means the process is at equilibrium, with no net tendency to run either way. $\Delta S(\text{universe}) < 0$ means the process is nonspontaneous as written; it can only run in reverse, or if driven by an outside influence in a coupled process.

**A5.** (a) False. Entropy measures dispersal of matter and energy, not heat released. Heat flow is one way entropy changes hands, but a gas expanding into a vacuum raises its entropy with no heat released at all. (b) False. The second law judges the universe, not the system. Freezing water has $\Delta S(\text{system}) < 0$ and is spontaneous below 0 °C because $\Delta S(\text{surroundings})$ is positive and larger. (c) False. It is close to zero, because two moles of gas form two moles of gas and the dispersal barely changes, but "barely" is not "exactly": close to zero is the honest claim. (d) False. A dissolving solid usually raises entropy, but a gas dissolving in a liquid lowers it, because the gas particles are captured from a large volume into the liquid.

**B1.** (a) Gas moles: 0 on the left, 1 on the right ($O_2$). $\Delta n(\text{gas}) = +1$, so $\Delta S > 0$. (b) Gas moles: 4 on the left (1 $N_2$ + 3 $H_2$), 2 on the right. $\Delta n(\text{gas}) = -2$, so $\Delta S < 0$. (c) Gas moles: 1 on each side ($O_2$ consumed, $CO_2$ formed; the carbon is a solid and does not enter the gas count). $\Delta n(\text{gas}) = 0$, so $\Delta S$ is close to zero. (d) Gas moles: 3 on the left (2 $H_2$ + $O_2$), 0 on the right, because the water is liquid. $\Delta n(\text{gas}) = -3$, so $\Delta S < 0$.

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**B2.** Most negative first: (d), then (b), then (c) close to zero, then (a) positive. Between the two negative cases, the size of the gas loss decides: (d) loses three moles of gas, (b) loses two, so (d) is more negative. Case (c) is not exactly zero because the gases are not identical in dispersal before and after (a mole of $O_2$ is replaced by a mole of $CO_2$ in the presence of a solid), so the entropy changes slightly even though the gas count does not.

**B3.** (a) Positive. The $Na^+$ and $Cl^-$ ions leave fixed positions in a rigid lattice and move freely through the water, so the matter of the system is far more dispersed. (b) Negative. The $CO_2$ particles give up the freedom of the gas phase, where each ranged over the whole container, and are confined within the liquid. (c) The direction of the volume change for the dissolving particles: the solid's ions gain freedom and space, while the gas's particles lose both. Dispersal gained means positive, dispersal lost means negative.

**B4.** (a) Positive: each gas spreads into the full volume of the container, so the particles are more dispersed even though nothing reacts. (b) Positive: the same particles occupy a larger volume, with more arrangements available. (c) Negative: the piston confines the gas to a smaller volume, reducing its dispersal. (d) Positive: warming spreads the sample's energy over more microstates. (e) Negative: cooling removes energy spread, and condensation then packs the particles from a gas into a liquid, both effects lowering entropy.

**B5.** (a) The sample at 1 atm: lower pressure means a larger volume per mole (deciding variable: pressure/volume). (b) The 1 mol sample: at equal temperature and pressure entropy is extensive (deciding variable: amount). (c) The sample at 600 K: higher temperature spreads energy over more microstates (deciding variable: temperature). (d) The 1 mol sample at 600 K and 1 atm: it wins on both variables at once, more material and more volume per particle, against 0.5 mol at higher pressure.

**B6.** (a) Positive: the $NH_4^+$ and $NO_3^-$ ions leave the ordered solid lattice and disperse through the solution. (b) Negative: the surroundings give up heat to the process, so their energy becomes less dispersed. (c) Spontaneity is decided by $\Delta S(\text{universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings})$. The positive system term from the dispersing ions is larger than the negative surroundings term, so the sum is positive and the process runs, even though it absorbs heat. (d) Positive, as the second law requires for any spontaneous process.

**C1.** (a) $\Delta S(\text{surroundings})$ must be greater than +80 J/K, so that the total exceeds zero. (b) $\Delta S(\text{universe}) = -80 + 80 = 0$ J/K. The process is at equilibrium: no net change runs in either direction. (c) $\Delta S(\text{universe}) = -80 + 95 = +15$ J/K $> 0$, so the process is spontaneous. (d) $\Delta S(\text{universe}) = +45 - 60 = -15$ J/K $< 0$, so the process does not run as written. Instead the reverse process runs spontaneously, since reversing both signs gives $\Delta S(\text{universe}) = +15$ J/K.

**C2.** (a) Negative: liquid water becomes an ordered solid, so the system's dispersal falls. (b) Positive: the heat released by the freezing water flows into the surroundings and disperses their energy over more microstates, raising their entropy. (c) Positive: the surroundings gain outweighs the

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system loss, and the second law requires ΔS(universe) > 0 for this spontaneous process. (d) Melting at −10 °C must have ΔS(universe) < 0. Freezing and melting swap the roles of initial and final states, so every entropy change reverses sign; since freezing gives a positive total, melting gives a negative one and cannot run on its own.

**C3.** (a) (i) Positive: a solid produces a gas, 0 moles of gas become 1. (ii) Negative: 4 moles of gas become 2. (iii) Close to zero: 2 moles of gas become 2 moles of gas. (iv) Negative: 3 moles of gas become 2. (b) Reaction (ii): it has the largest decrease in gas moles, Δn(gas) = −2, against −1 for reaction (iv). (c) The claim is wrong twice over. First, the mole change in (iv) is real, 3 becoming 2, so the reaction has ΔS < 0, not zero. Second, molecular complexity compares the standard molar entropies of substances; it does not cancel a change in the number of gas particles, which is the dominant effect on a reaction's ΔS. (d) Reaction (iii). Its gas count is unchanged, so the dispersal of the system barely changes, but the reactants and products are different gases with slightly different dispersals, so ΔS is small rather than identically zero: "closest to zero" is the precise statement.

**Continue Revising**

Topic 9.1 Revision Notes

Topic 9.1 Quiz: Introduction to Entropy

Previous Worksheet: Topic 8.10 Buffer Capacity

Next Worksheet: Topic 9.2 Absolute Entropy and Entropy Change

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