Entropy, Enthalpy, and Free Energy

The equation relating these factors is: $\Delta G = \Delta H - T\Delta S$, where G is free energy, H is enthalpy, S is entropy, and T is temperature (in Kelvin). Although temperature values will always be positive, entropy, enthalpy, and free energy values can be positive or negative.

For a given process, a quantitative value for each factor can be calculated using the known values of the factors for each reactant involved (see Table 1) according to the general equation $\Delta X°_{rx} = \Sigma X°(\text{products}) - \Sigma X°(\text{reactants})$. See if the following activity helps you better understand what these quantities really mean.

Table 1

	ΔH° (kJ/mol)	S° (J/K mol)	ΔG° (kJ/mol)
HCO_3^-	-691.1	94.94	-587.1
H^+	0	0	0
H_2O (l)	-285.8	69.9	-237.2
CO_2 (g)	-393.5	213.6	-394.4

Materials

- vinegar
- baking soda
- thin-walled cup
- tablespoon measure
- teaspoon measure

Exploration

Step 1 Put about 2 tablespoons vinegar in a cup. Add a teaspoon or two of baking soda to the cup.

(a) What do you observe through sight, sound, and touch?

(b) What kind of change is occurring?

(c) What are the formulas of the 2 major components of vinegar and of the one component of baking soda?

(d) Write the overall equation and the net ionic equation for the process.

Step 2 (a) Define entropy and the significance of the sign of its value.

(b) Based on your observations, explain the entropy change for the system observed in Step 1.

(c) Use the entropy data from Table 1 to calculate the entropy change for the net ionic equation from Step 1.

(d) Is your calculated value consistent with your conclusions from observation? Explain.

Step 3 (a) Define enthalpy and the significance of the sign of its value.
(b) Based on your observations, explain the enthalpy change for the system observed in Step 1.
(c) Use the enthalpy data from Table 1 to calculate the enthalpy change for the net ionic equation from Step 1.
(d) Is your calculated value consistent with your conclusions from observation? Explain.

Step 4 (a) Define free energy and the significance of the sign of its value. There are two ways to calculate the free energy of the system observed in Step 1 from the available data.
(b) Calculate free energy both ways using the 2 equations and Table 1 data and calculated values from Steps 2 and 3 (assume that the reaction was performed at 25°C).
(c) Compare the values.
(d) What do these values tell you about the type of change that occurred? Explain.
(e) A change in what condition would make which one of these two equations invalid? Explain.

Step 5 Now think about the process of an ice cube melting at room temperature.
(a) What kind of change is this?
(b) Without doing any calculations, predict the signs of entropy, enthalpy, and free energy and explain your reasoning.

Challenge

Based on the consideration of two real processes, what can be concluded about how the sign and/or magnitude of entropy and enthalpy affect free energy? Answer the challenge by considering the equation: $\Delta G = \Delta H - T\Delta S$, to complete Table 2:

Table 2

ΔH	ΔS	ΔG
positive	negative	
negative	positive	
large and negative	small and negative	
small and positive	large and positive	

Entropy, Enthalpy, and Free Energy

Concepts

entropy, enthalpy, free energy, spontaneity

Expected Student Responses to Exploration

Step 1 (a) Bubbles are both seen and heard and an observant student should notice that the system feels cooler.

(b) A chemical change is occurring.

(c) The major components of vinegar are water, H_2O (solvent), and acetic acid, $HC_2H_3O_2$; baking soda is sodium bicarbonate, $NaHCO_3$).

(d) The overall equation is:
$NaHCO_3(aq) + HC_2H_3O_2(aq) \rightarrow H_2O(l) + CO_2(g) + NaC_2H_3O_2(aq)$
The net ionic equation is:
$HCO_3^- + H^+ \rightarrow H_2O(l) + CO_2(g)$

Step 2 (a) Entropy is a measure of disorder. A positive change in entropy value indicates that the system has become more disordered; a negative change in entropy value indicates that the system has become more ordered.

(b) The entropy of the system in Step 1 increased because a gas was produced; a gas is far more disordered than a liquid.

(c) The calculated value is 188.6 J/K.

(d) The value is consistent; a positive value indicates disorder has increased.

Step 3 (a) Enthalpy is a measure of heat energy. For an endothermic process (the system absorbs heat from the surroundings), the enthalpy is positive. For an exothermic process (the system releases heat to the surroundings), the enthalpy is negative.

(b) Based on the system getting colder as a result of the chemical change, the process is exothermic and the enthalpy is negative.

(c) The calculated value is 11.8 kJ.

(d) The value is logical; a positive value indicates the reaction is endothermic.

Step 4 (a) Free energy is the amount of energy that is available to do work. A negative value indicates the process is spontaneous; a positive value indicates it is not.

(b) Using free energy values gives -44.5 kJ; using entropy and enthalpy values gives -44.4 kJ.

(c) The values are essentially equivalent.

(d) The negative free energy values indicate the process is spontaneous.

(e) A change in temperature would mean that only the equation $\Delta G = \Delta H - T\Delta S$ could be used; the other equation only applies for reactions at standard conditions (25°C).

Step 5 (a) This is a physical change.

(b) We know that an ice cube melts at room temperature. It is, therefore, a spontaneous process; free energy is negative. The process of a solid transforming to a liquid involves an increase in disorder; entropy is positive. Heat is taken in, so the process is endothermic; enthalpy is positive.

Expected Student Answer to Challenge

ΔH	ΔS	ΔG
positive	negative	positive
negative	positive	negative
large and negative	small and negative	positive
small and positive	large and positive	negative

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