



# THERMODYNAMICS

GIBBS FREE ENERGY (G) AND SPONTANEITY

CHEMISTRY 165 // SPRING 2020

# PRACTICE PROBLEM 1

Consider the sublimation of solid dry ice spontaneously at 25 °C:  $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$

Determine the signs of the following thermodynamic properties for this process.

— *answer* —

	$\Delta H$	$\Delta S$	$\Delta G$
System			
Surroundings			n/a

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— *answer* —

Because the process occurs spontaneously at 25 °C, the  $\Delta G_{\text{sys}} < 0$  and also  $\Delta S_{\text{univ}} > 0$ .

Now work through the other thermodynamic properties.

	$\Delta H$	$\Delta S$	$\Delta G$
System	>0	>0	<0
Surroundings	<0	<0	n/a
Details	Heat is required to sublime from the solid to gas phase. This process is endothermic, and the temperature of the surroundings decreases.	Entropy increase going from the solid to gas phase (greater disorder). $\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} < 0$	At 25 °C, this process is spontaneous and $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$

## PRACTICE PROBLEM 2

Using the following thermodynamic properties, determine whether the dissolution of (a) 1 mole of NaBr or (b) 1 mole of NaI in water is more favorable at 298 K.

	$\Delta H^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	$\Delta S^\circ \left( \frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$
NaBr	-0.86	57
NaI	-7.5	74

— answer —

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— answer —

We can calculate the Gibbs free energy change for both dissolution processes ( $\Delta G_{\text{rxn}}^\circ$ ) using  $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ$ .

$$\Delta G_{\text{NaBr}}^\circ = -0.86 \frac{\text{kJ}}{\text{mol}} - (298 \text{ K}) \left( 0.057 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = -18 \frac{\text{kJ}}{\text{mol}}$$
$$\Delta G_{\text{NaI}}^\circ = -7.5 \frac{\text{kJ}}{\text{mol}} - (298 \text{ K}) \left( 0.074 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = -30. \frac{\text{kJ}}{\text{mol}}$$

The more favorable reaction is the one that is more spontaneous, which is the one with the more negative value of  $\Delta G_{\text{rxn}}^\circ$ .

Therefore, **the dissolution of 1 mole of NaI in water is more favorable** than the dissolution of 1 mole of NaBr in water.

## PRACTICE PROBLEM 3



- (a) Calculate the  $\Delta G^\circ$  for the reaction using the following standard Gibbs free energies of formation ( $\Delta G_f^\circ$ ).
- (b) What does the sign and magnitude of the  $\Delta G_f^\circ$  value say about the favorability and spontaneity of this reaction?

	$\text{N}_2\text{O}_3 (\text{g})$	$\text{NO} (\text{g})$	$\text{NO}_2 (\text{g})$
$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	139.5	86.6	51.3

— answer —



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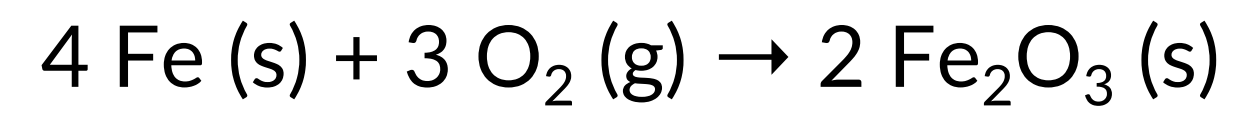
	$\text{N}_2\text{O}_3 (\text{g})$	$\text{NO} (\text{g})$	$\text{NO}_2 (\text{g})$
$\Delta G_f^\circ \left( \frac{\text{kJ}}{\text{mol}} \right)$	139.5	86.6	51.3

— answer —

$$\begin{aligned} \text{(a)} \quad \Delta G_{\text{rxn}}^\circ &= \sum n_{\text{prod}} \Delta G_{f,\text{prod}}^\circ - \sum n_{\text{react}} \Delta G_{f,\text{react}}^\circ \\ &= \left[ (1 \text{ mol NO}) \times \left( 86.6 \frac{\text{kJ}}{\text{mol}} \right) + (1 \text{ mol NO}_2) \times \left( 51.3 \frac{\text{kJ}}{\text{mol}} \right) \right] - (1 \text{ mol N}_2\text{O}_3) \times \left( 139.5 \frac{\text{kJ}}{\text{mol}} \right) \\ \Delta G_{\text{rxn}}^\circ &= -1.6 \text{ kJ} \end{aligned}$$

- (b) The reaction is **spontaneous** because  $\Delta G_{\text{rxn}}^\circ < 0$ ; however, because the magnitude of the  $\Delta G_{\text{rxn}}^\circ$  is relatively small, this reaction is only **slightly products favored** (right-ward direction).

## PRACTICE PROBLEM 4

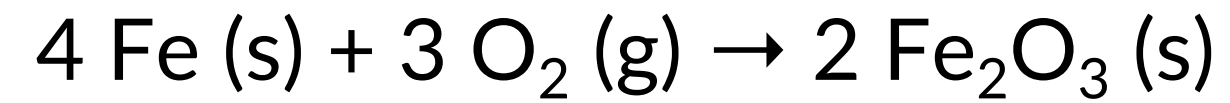


Given that this reaction is exothermic, how does the spontaneity of this reaction depend on temperature?

— *answer* —



## PRACTICE PROBLEM 4



Given that this reaction is exothermic, how does the spontaneity of this reaction depend on temperature?

— *answer* —

First, recall the Gibbs free energy relationship:  $\Delta G = \Delta H - T\Delta S$

Second, recall that spontaneous reactions have  $\Delta G < 0$ .

Now, let's analyze the reaction and data.

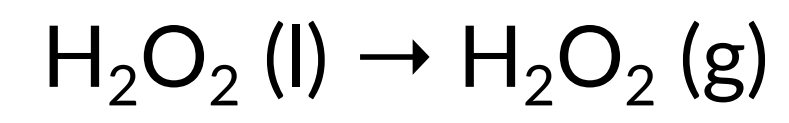
They tell us that the reaction is exothermic, so we know that  $\Delta H < 0$ .

What about the entropy change for the reaction? Going from reactants to products, we are losing 3 moles of gas (very disordered or higher entropy) and forming 2 moles of solid (less disorder and lower entropy), so we expect that  $\Delta S < 0$ .

Invoking the Gibbs free energy relationship above, **this reaction will be spontaneous ( $\Delta G < 0$ ) at low temperatures.**

At high temperatures, the  $T\Delta S$  term becomes very large and negative; hence,  $\Delta G > 0$  at high temperatures.

## PRACTICE PROBLEM 5



If the  $\Delta H^\circ = 51.5 \text{ kJ}$  and  $\Delta S^\circ = 123.1 \text{ J/K}$ , estimate the boiling point of hydrogen peroxide at atmospheric pressure.

— *answer* —

## PRACTICE PROBLEM 5



If the  $\Delta H^\circ = 51.5 \text{ kJ}$  and  $\Delta S^\circ = 123.1 \text{ J/K}$ , estimate the boiling point of hydrogen peroxide at atmospheric pressure.

— *answer* —

First, recall the Gibbs free energy relationship:  $\Delta G = \Delta H - T\Delta S$

Second, recall that at the boiling point (or any phase change), the two states are in equilibrium and  $\Delta G = 0$ .

From the given information we can calculate the standard Gibbs free energy change as

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

We can express the nonstandard Gibbs free energy change (since at boiling the temperature is nonstandard) as

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

In most reactions, the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change much with temperature. Therefore:

$$\Delta G = 0 \approx \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$
$$= \frac{51.5 \text{ kJ}}{0.1231 \frac{\text{J}}{\text{K}}}$$

$$T = 418.4 \text{ K}$$