

Second Law of Thermodynamics

First Law:

the total energy of the universe is a constant

Second Law:

The entropy of the universe increases in a spontaneous process, and remains unchanged in a process at equilibrium

Entropy and the second law

A process is spontaneous if ΔS_{univ} is positive

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

A process is at equilibrium if:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = 0$$

Therefore we need to consider how the entropy of the system and the surroundings change during a process

Entropy changes in the System

Entropy changes in the System

ΔS_{system} is **+** if disorder increases

ΔS_{system} is **-** if products are more ordered than reactants

Can be calculated from tables of thermodynamic values

$$\Delta S^{\circ}_{\text{rxn}} = \sum n S^{\circ} (\text{products}) - \sum m S^{\circ} (\text{reactants})$$

We can often make good guesses as to the sign of ΔS_{system}

Entropy changes in the System

Calculate the standard entropy change for:



qualitative prediction: 2 moles of gas on the right, 3 on the left ; the products are more ordered than reactants; the sign of

ΔS° is -

Entropy changes in the System

If a reaction produces excess gas ΔS_{system} is +

If a reaction produces no net change in gas molecules ΔS_{system} may be (+) or (-) but the change will have a small value

General Rule: a reaction that increases the total number of molecules or ions will increase ΔS_{system}

Example:

Calculate the standard entropy change for:



S° (reactants)

$$\begin{aligned} & 2 \text{ mol}(197.9 \text{ J/K}\cdot\text{mol}) \\ & + 1 \text{ mol}(205 \text{ J/K}\cdot\text{mol}) \\ & = 600.8 \text{ J/K} \end{aligned}$$

S° (products)

$$\begin{aligned} & 2 \text{ mol}(213.6 \text{ J/K}\cdot\text{mol}) \\ & = 427.2 \text{ J/K} \end{aligned}$$

$$\Delta S^\circ_{\text{rxn}} = 427.2 \text{ J/K} - 600.8 \text{ J/K}$$

$$\Delta S^\circ_{\text{rxn}} = -173.6 \text{ J/K}$$

Third Law of Thermodynamic and Absolute Entropy

the entropy of a perfect crystalline substance is zero at the absolute zero of temperature : 0 K (-273° C)

important in the determination of absolute entropy values

Entropy changes in the surroundings

Entropy changes in the surroundings

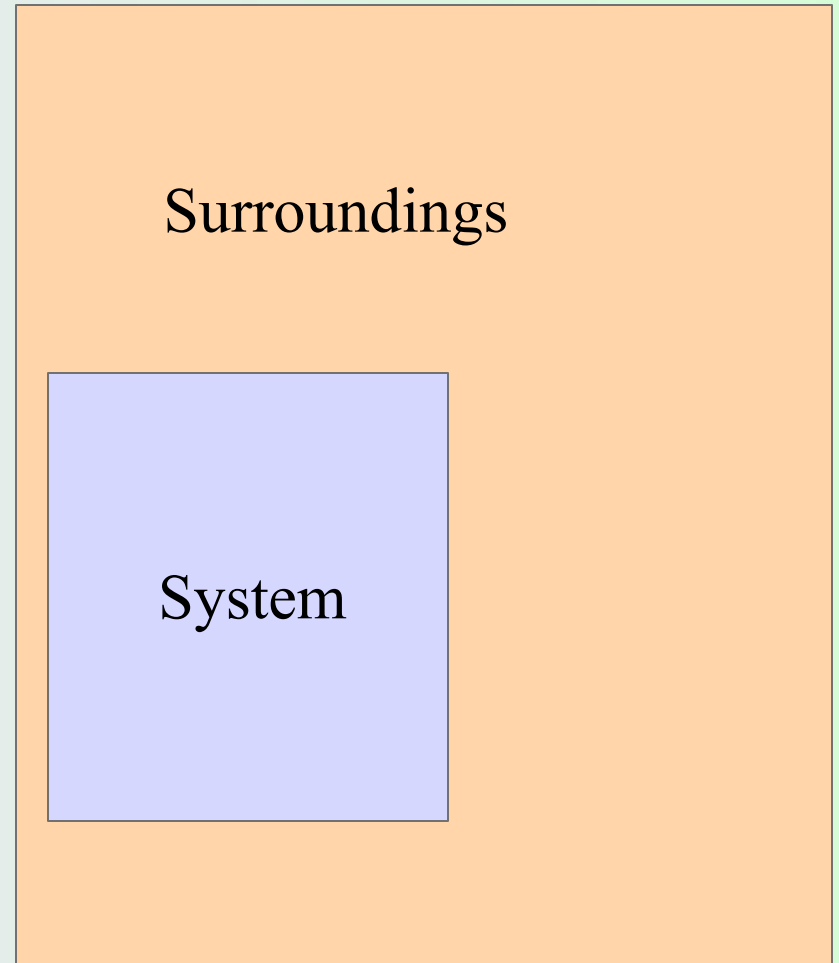
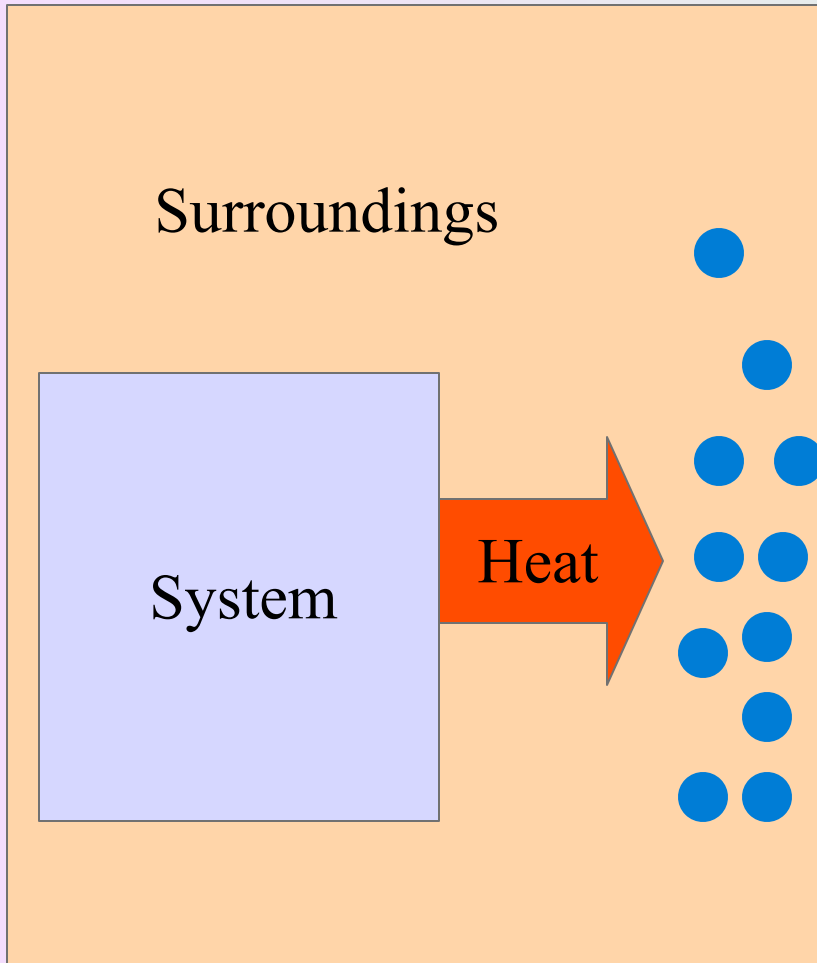
How are surroundings affected by heating and cooling

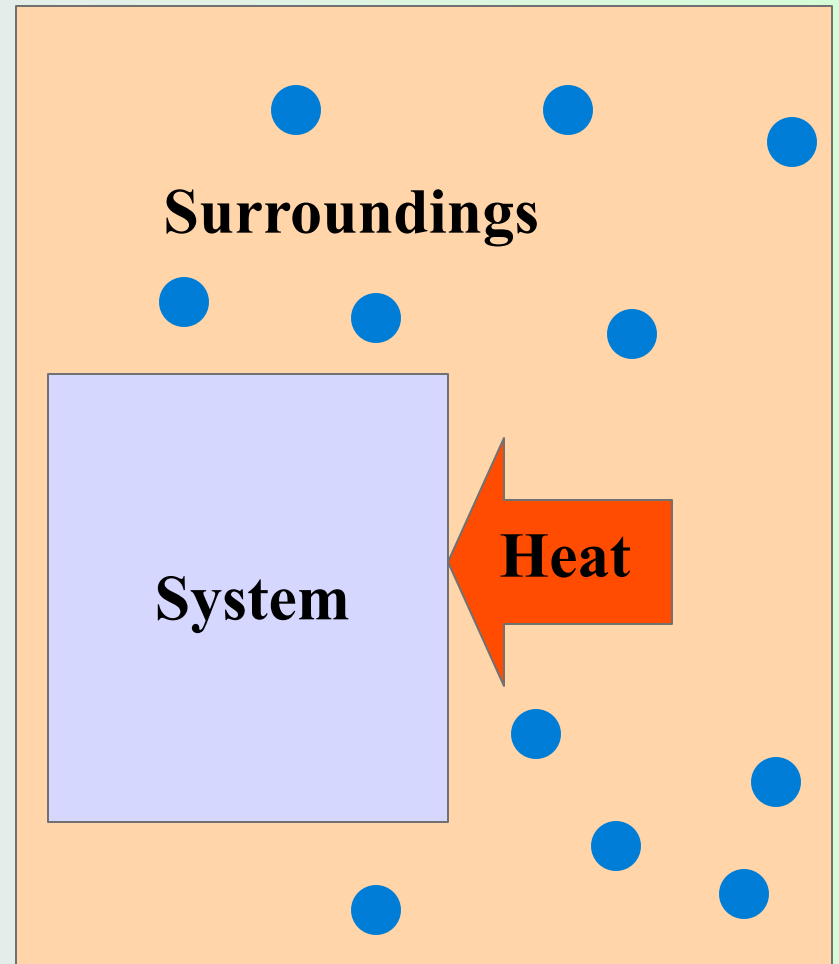
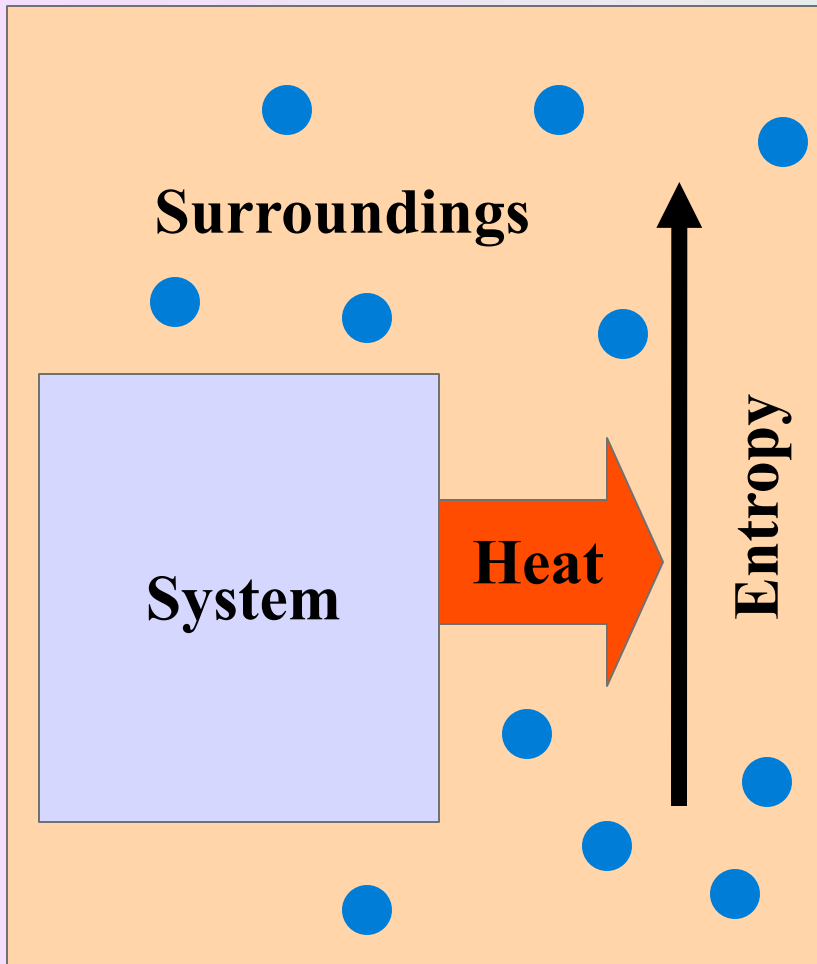
exothermic reactions increases entropy of surroundings

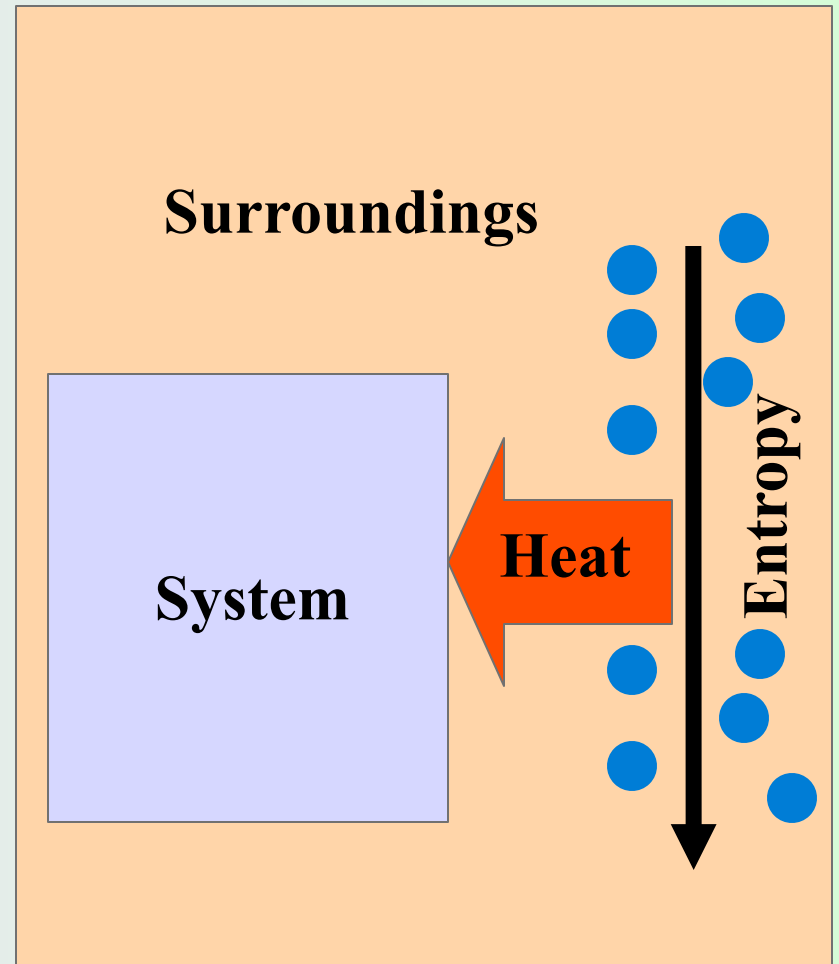
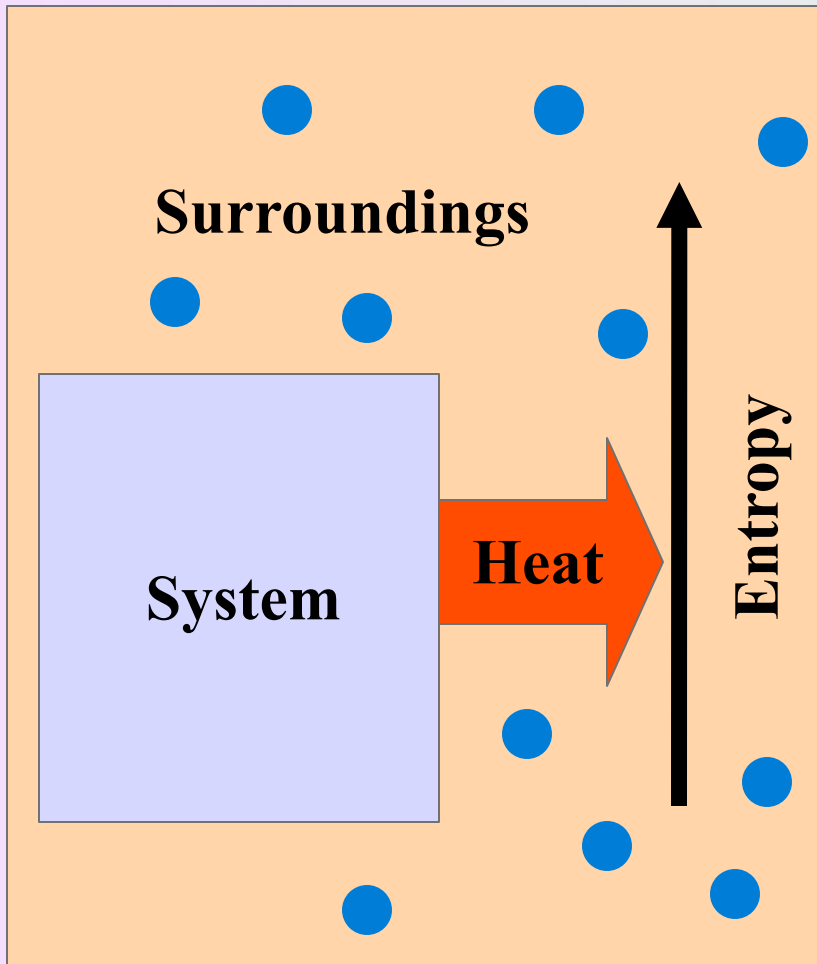
endothermic reactions decrease entropy of surroundings

$$\Delta S_{\text{surr}} = \frac{q}{T}$$

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







What are the possibilities?

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{univ}} \quad \text{spontaneous?}$$

+

+

+

yes

-

-

-

no

+

-

?

-

+

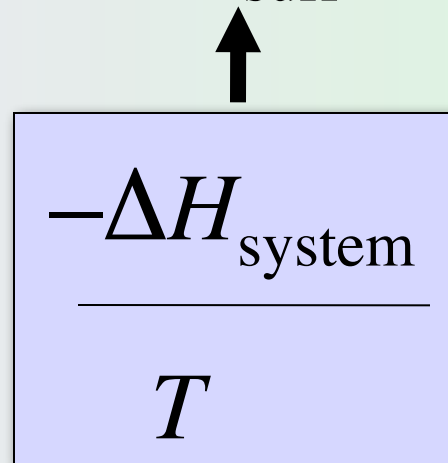
?

Spontaneity and temperature

a reaction may be spontaneous at one temperature and nonspontaneous at a different temperature

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$





The diagram shows a light blue rectangular box with a black border. Inside the box, the equation $\frac{-\Delta H_{\text{system}}}{T}$ is written. A black arrow points upwards from the top center of the box to the ΔS_{surr} term in the equation above.

Gibbs Free Energy

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

we study the system; therefore reference “surroundings” in terms of the system

$$\Delta S_{\text{universe}} = -\Delta H_{\text{system}} / T + \Delta S_{\text{system}}$$

$$T\Delta S_{\text{universe}} = -\Delta H_{\text{system}} + T\Delta S_{\text{system}}$$

$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

$$\Delta G = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

Gibbs Free Energy

Free Energy (ΔG) is a measure energy available to do work.

a release of free energy during a chemical reaction is spontaneous

Criterion for spontaneity is the Gibbs free energy change

at constant temperature and pressure, if

ΔG_{system} is

negative, the reaction is **spontaneous**

positive, the reaction is not **spontaneous**

zero, the system is at **equilibrium**

Standard Free-Energy Changes

Standard Free Energies of Formation

the change in free energy that accompanies the formation of 1 mole of a substance from its constituent elements at standard conditions

$$\Delta G^{\circ} = \text{kJ}$$

$$\Delta G_f^{\circ} = \text{kJ/mol}$$

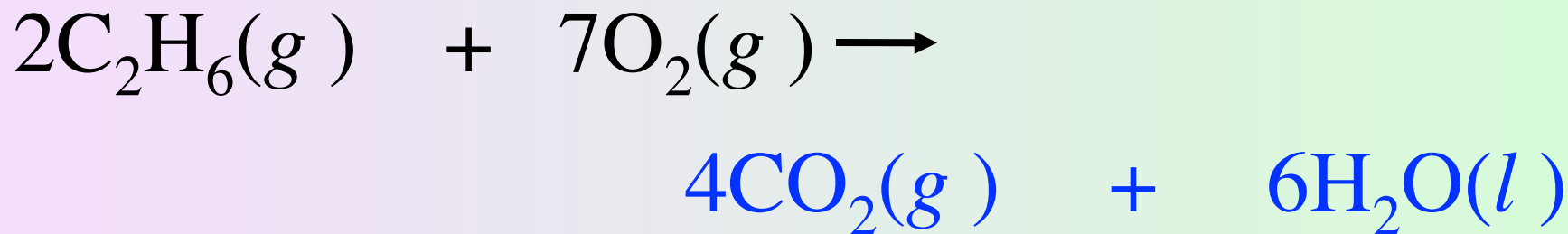
From Standard Free Energies of Formation

$$\Delta G^{\circ}_{\text{rxn}} = \sum n \Delta G^{\circ}_f (\text{products}) - \sum m \Delta G^{\circ}_f (\text{reactants})$$

the standard free energies of formation of any element in its stable form equals zero

Example:

Calculate the standard free-energy changes for the following reaction at 25°C :



$$2\text{mol}(-32.9 \text{ kJ/mol}) + 7\text{mol}(0 \text{ kJ/mol})$$

$$4\text{mol}(-394.4 \text{ kJ/mol}) + 6\text{mol}(-237.2 \text{ kJ/mol})$$

$$-66 \text{ kJ}$$

$$-3001 \text{ kJ}$$

$$\Delta G^{\circ} = -3001 - (-66) = -2935 \text{ kJ}$$

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

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

ΔH negative and ΔS positive; reaction spontaneous at all temperatures

ΔH positive and ΔS negative; reaction can't be spontaneous at any temperature

ΔH positive and ΔS positive; increasing temperature favors spontaneity

ΔH negative and ΔS negative; increasing temperature works against spontaneity

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

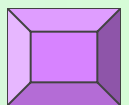
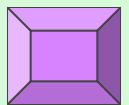
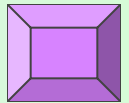
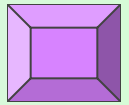
ΔH negative and ΔS positive; reaction spontaneous at all temperatures

ΔH positive and ΔS negative; reaction can't be spontaneous at any temperature

ΔH positive and ΔS positive; increasing temperature favors spontaneity

ΔH negative and ΔS negative; increasing temperature works against spontaneity

Click for example



Endothermic dissolution: at 25°C (298 K)



$$\Delta H_f^\circ \quad -315.4 \text{ kJ/mol} \quad -132.8 \text{ kJ/mol} \quad -167.2 \text{ kJ/mol}$$

$$S^\circ \quad 94.6 \text{ J/mol K} \quad 112.8 \text{ J/mol K} \quad 56.5 \text{ J/mol K}$$

Endothermic dissolution: at 25 ° C (298 K)



$$\Delta H^\circ_{rxn} =$$

$$[-132.8 \text{ kJ/mol} + (-167.2 \text{ kJ/mol})] - (-315.4 \text{ kJ/mol})$$
$$= 15.4 \text{ kJ/mol}$$

$$\Delta S^\circ =$$

$$[112.8 \text{ J/mol K} + 56.5 \text{ J/mol K}] - (94.6 \text{ J/mol K})$$
$$= 74.7 \text{ J/mol K}$$
$$= .0747 \text{ kJ/mol K}$$

Endothermic dissolution: at 25 ° C (298 K)



$$\Delta H^{\circ}_{rxn} = 15.4 \text{ kJ/mol}$$

$$\Delta S^{\circ} = .0747 \text{ kJ/mol K}$$

$$T = 298 \text{ K}$$

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

$$\Delta G^{\circ} = 15.4 \text{ kJ/mol} - 298 \text{ K} (.0747 \text{ kJ/mol K})$$

$$\Delta G^{\circ} = -6.86$$

Endothermic dissolution: at 25 ° C (298 K)



$$\Delta H_f^\circ \quad -315.4 \text{ kJ/mol} \quad -132.8 \text{ kJ/mol} \quad -167.2 \text{ kJ/mol}$$

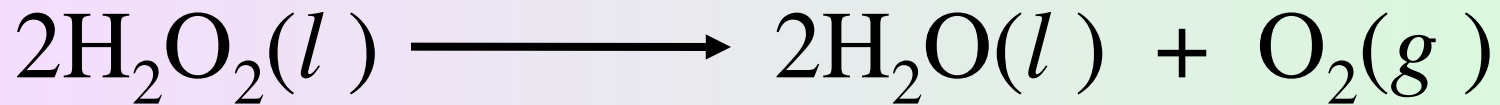
$$S^\circ \quad 94.6 \text{ J/mol K} \quad 112.8 \text{ J/mol K} \quad 56.5 \text{ J/mol K}$$

$$\Delta G_f^\circ \quad -203.9 \text{ kJ/mol} \quad -79.5 \text{ kJ/mol} \quad -131.2 \text{ kJ/mol}$$

$$\Delta G^\circ_{rxn} = -6.8 \text{ kJ/mol}$$

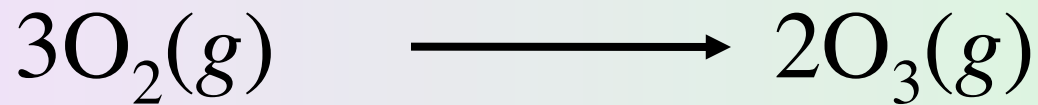
Example

ΔH negative and ΔS positive; reaction spontaneous at all temperatures



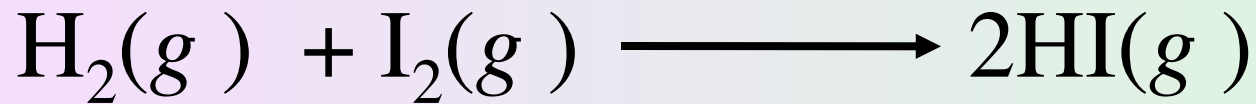
Example

ΔH positive and ΔS negative; reaction can't be spontaneous at any temperature



Example

ΔH positive and ΔS positive; increasing temperatures favors spontaneity



Example

ΔH negative and ΔS negative; increasing temperatures works against spontaneity

