

## Chapter 16



### Thermodynamics

#### GCC CHM152



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## Thermodynamics

- You are responsible for Thermo concepts from CHM 151. You may want to review Chapter 5, specifically sections 1-3.
- **Thermodynamics: Study of energy changes in chemical reactions and physical processes.**
- Thermodynamics allows us to determine IF a reaction will occur.
- It also tells us the direction and extent of a reaction.
- It does not tell us how fast a reaction occurs (kinetics tell us this!)

## Thermochemistry Review

**1<sup>st</sup> Law of Thermodynamics:** Energy is conserved. Energy can be converted from one form to another but it cannot be created or destroyed.

- ◆ If a system gives off heat, the surroundings must absorb it (and vice versa).
- ◆ Heat flow (enthalpy,  $\Delta H$ ) is defined with reference to the system
  - **System absorbs heat,  $\Delta H > 0$ , endothermic**
  - **System gives off heat,  $\Delta H < 0$ , exothermic**

## Predicting sign for $\Delta H_{\text{rxn}}^{\circ}$

Predict whether the following are endothermic (need heat) or exothermic (release heat):

- ◆ Decomposition +
- ◆ Acid-Base Neutralization -
- ◆ Combustion -
- ◆ Melting +
- ◆ Freezing -
- ◆ Boiling +

**Remember breaking bonds requires energy = endo  
but making new bonds releases energy = exo.**

## Calculating $\Delta H_{\text{rxn}}^{\circ}$

The  $^{\circ}$  symbol refers to the **standard state**, 1.00 atm pressure, 25.0°C, 1.00 M for solutions

$\Delta H_f^{\circ}$  = **Standard Molar Enthalpy of Formation**

**The enthalpy change when 1 mole of a compound is formed from its elements in their standard states.**

- ◆ Appendix G lists values for  $\Delta H_f^{\circ}$ ,  $\Delta G_f^{\circ}$  and  $S^{\circ}$
- ◆  $\Delta H_f^{\circ} = 0$  for an element in its most stable form
- ◆ Know most stable forms for the elements!
- ◆  $\Delta H_f^{\circ}$  units: kJ/mol

$$\Delta H_{\text{rxn}}^{\circ} = \sum n \cdot \Delta H_f^{\circ} (\text{products}) - \sum n \cdot \Delta H_f^{\circ} (\text{reactants})$$

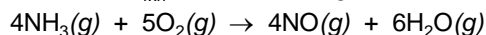
- $n$  = moles (coefficient in balanced reaction)

## Heat of formation rxn & $\Delta H^\circ_{\text{rxn}}$

Write heat of formation reaction for  $\text{H}_2\text{O}(l)$ .

- Product = 1 mol  $\text{H}_2\text{O}(l)$
- Reactants = elements in most stable form
  - ♦  $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$

Calculate  $\Delta H^\circ_{\text{rxn}}$  for the following reaction.



$$\Delta H^\circ_f [\text{NO}(g)] = 90.2 \text{ kJ/mol}; \Delta H^\circ_f [\text{H}_2\text{O}(g)] = -241.8 \text{ kJ/mol}$$

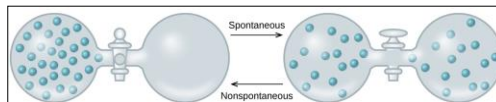
$$\Delta H^\circ_f [\text{NH}_3(g)] = -46.1 \text{ kJ/mol}; \Delta H^\circ_f [\text{O}_2(g)] = ?$$

**Answer:  $\Delta H^\circ_{\text{rxn}} = -905.6 \text{ kJ}$**

## Spontaneous Processes

A **spontaneous process** proceeds on its own without any external influence. The reverse of a spontaneous process is always nonspontaneous –it does not occur naturally.

- ♦ Consider the expansion of a gas into a vacuum. This happens spontaneously. The reverse process does not!



## Spontaneous Chemical Reactions

Spontaneous processes

- ♦ hot object cools
- ♦ Ice melts at  $T > 0^\circ\text{C}$
- ♦ iron rusts
- ♦ sodium reacts with  $\text{H}_2\text{O}$
- Note that spontaneous does not mean fast!
  - ♦ Rusting of iron is spontaneous but occurs slowly!
- What makes a process spontaneous?
  - ♦ Spontaneity is determined by both the enthalpy and entropy of a reaction.

## Enthalpy, Entropy and Spontaneity

Nature tends toward state of lower energy.

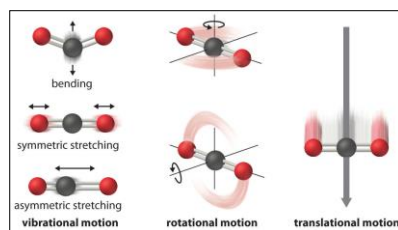
- Many spontaneous processes are exothermic (e.g. combustion reactions have  $\Delta H < 0$ ), but some spontaneous processes are endothermic (e.g. ice melting has  $\Delta H > 0$ ).
- Nature tends to become more disordered or random.
- Entropy of a system typically increases,  $\Delta S > 0$  ( $+\Delta S = \text{increase in disorder}$ )
- Example: an office naturally becomes more messy over time.

## Entropy (S)

Entropy is a measure of disorder or randomness.

- Units of Entropy:  $\frac{\text{J}}{\text{K} \cdot \text{mol}}$
- $S^\circ$ : standard molar entropy of an element in its most stable form is not zero!

## Entropy of Molecules

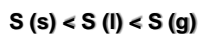
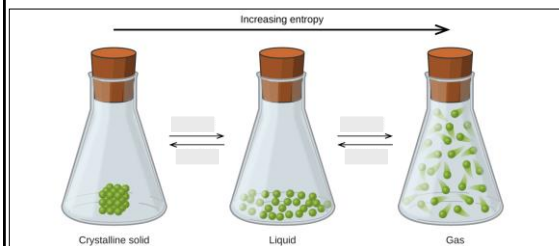


The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration. The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy.

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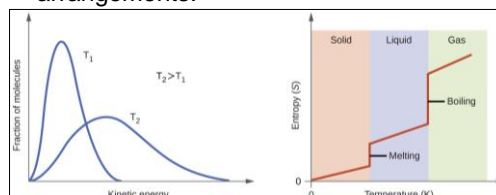
## Which has the greater entropy?

Solid, liquid or gas? (ice, water, or steam)



## Entropy and temperature

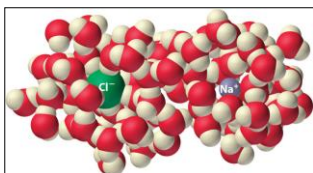
- Consider gases at different temperatures
- High T: More motion & higher kinetic energy so there are more possible arrangements.



## Entropy and solubility

Dissolving a solute usually increases entropy since a solution has more possible arrangements and is more dispersed but some ionic compounds have a negative entropy change upon dissolution.

Ionic compounds: entropy can decrease or increase



## Entropy Summary

- Temperature changes
  - ♦ Increase:  $\Delta S > 0$  (more energy, more positions, more possible arrangements)
- Phase changes
  - ♦ Boiling, melting:  $\Delta S > 0$
- Creating more moles
  - ♦  $\Delta S > 0$
- Salts dissolving:  $\Delta S$  +/- but usually
- Also entropy usually  $\uparrow$  as complexity of molecule increases.

## Predict Entropy change

Predict whether entropy increases ( $\Delta S > 0$ ) or decreases ( $\Delta S < 0$ ) for the following processes. **Explain why!**

- $2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(l)$
- $\text{KBr}(s) \rightarrow \text{K}^+(aq) + \text{Br}^-(aq)$
- $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$
- $\text{I}_2(s) \rightarrow \text{I}_2(g)$
- $\text{PCl}_5(s) \rightarrow \text{PCl}_3(l) + \text{Cl}_2(g)$

## Answers

- $2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(l)$ :
  - ♦  $\Delta S < 0$ ; fewer particles, phase change
- $\text{KBr}(s) \rightarrow \text{K}^+(aq) + \text{Br}^-(aq)$ :
  - ♦  $\Delta S > 0$ ; more particles/phase change
- $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$ :
  - ♦  $\Delta S < 0$ ; fewer particles/phase change
- $\text{I}_2(s) \rightarrow \text{I}_2(g)$ :
  - ♦  $\Delta S > 0$ ; phase change
- $\text{PCl}_5(s) \rightarrow \text{PCl}_3(l) + \text{Cl}_2(g)$ :
  - ♦  $\Delta S > 0$ ; more particles/phase changes

## Standard Molar Entropy

**3<sup>rd</sup> Law of Thermodynamics:** The entropy of a perfectly ordered crystalline substance at 0 K is zero.

- This allows us to calculate entropy (S) and changes in entropy ( $\Delta S$ ); unlike enthalpy where we can only measure changes!

**Standard Molar Entropies** (Table 16.2) - entropy of 1 mole of a pure substance at 1 atm pressure and 25°C (J/mol·K)

$$\Delta S^\circ_{\text{rxn}} = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$$

## Standard Entropy Values ( $S^\circ$ )

Which phase has the lowest entropy? Highest?

Substance	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Substance	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
C (s, diamond)	2.38	H (g)	114.6
C (s, graphite)	5.740	H <sub>2</sub> (g)	130.57
Al (s)	28.3	CH <sub>4</sub> (g)	186.3
Al <sub>2</sub> O <sub>3</sub> (s)	50.92	HCl (g)	186.8
BaSO <sub>4</sub> (s)	132.2	H <sub>2</sub> O (g)	188.8
		CO (g)	197.7
H <sub>2</sub> O (l)	70.0	CO <sub>2</sub> (g)	213.8
Hg (l)	75.9	C <sub>2</sub> H <sub>4</sub> (g)	219.3
H <sub>2</sub> O <sub>2</sub> (l)	109.6	C <sub>2</sub> H <sub>6</sub> (g)	229.5
Br <sub>2</sub> (l)	152.23	CH <sub>3</sub> OH (g)	239.9
CCl <sub>4</sub> (l)	214.4	CCl <sub>4</sub> (g)	309.7

**Note:** The standard entropy for a pure element in its most stable form is **NOT** zero (like for  $\Delta H^\circ$ ).

## Entropy Change for a Reaction

Calculate  $\Delta S^\circ_{\text{rxn}}$  for  $2\text{Na}(s) + \text{Cl}_2(g) \rightleftharpoons 2\text{NaCl}(s)$

**$S^\circ$  values:** Na(s) = 51.05 J/mol·K, Cl<sub>2</sub>(g) = 223.0 J/mol·K, NaCl(s) = 72.38 J/mol·K

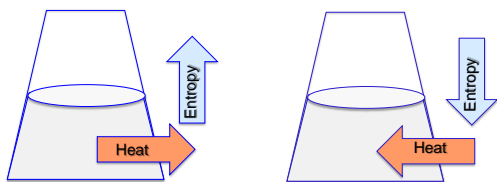
- $\Delta S^\circ_{\text{rxn}} = -180.3 \text{ J/K}$
- Entropy change is < 0. There is more order due to the phase change.

## 2<sup>nd</sup> Law of Thermodynamics

- 2<sup>nd</sup> Law of Thermodynamics:** in any spontaneous process, the **total** entropy of a **system and its surroundings** always increases. (system = reaction)
- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- $\Delta S_{\text{total}} > 0$ , the reaction is spontaneous
- $\Delta S_{\text{total}} < 0$ , the reaction is nonspontaneous
- $\Delta S_{\text{total}} = 0$ , the reaction is at equilibrium
- All reactions proceed spontaneously in a direction that increases the entropy of the system plus the surroundings.

## 2<sup>nd</sup> Law of Thermodynamics

- $\Delta S_{\text{sys}}$  is the entropy change for the reaction that we just calculated.
- $\Delta S_{\text{surr}}$  is related to the enthalpy of the system; if Heat flows into the surroundings then their entropy increases due to increased motion.



## Calculating $\Delta S_{\text{surr}}$

- Exothermic: heat flows from system to surroundings, surroundings have more energy = more disorder. (Hotter particles have more motion)
  - $\Delta S_{\text{surr}} > 0$  when exothermic:  $\Delta H < 0$
- Endothermic: heat flows into system from surroundings, surroundings have less energy which gives them more order.
  - $\Delta S_{\text{surr}} < 0$  when endothermic:  $\Delta H > 0$
- Therefore:  $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$
- $\Delta S_{\text{Tot}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$

## Gibbs free energy (G) or free energy

G is the maximum amount of energy available to do work on the surroundings.

- ◆ Takes into account enthalpy and entropy to predict spontaneity of a reaction.
- $\Delta G = \Delta H - T\Delta S$  ( $\Delta G$  units: kJ/mol)
  - ◆ T must be in Kelvin! Watch units!
  - ◆ The actual amount of work ( $w_{\max}$ ) obtained is always less than the maximum available because of energy lost in carrying out a process (given off as heat, light, sound, etc. energy).
- **In any spontaneous process (constant T and P), the free energy of the system always decreases!**

## Predicting sign for Free Energy Change

- $\Delta G < 0 \Rightarrow$  **Spontaneous process**
- $\Delta G > 0 \Rightarrow$  **Nonspontaneous process**
- $\Delta G = 0 \Rightarrow$  **Process is at equilibrium**

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

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Free Energy sign is T dependent when enthalpy and entropy have same sign!

- Notice that the  $T\Delta S$  term is **temperature dependent**. Temperature plays a part in predicting spontaneity.
  - ◆ **Endothermic** processes are spontaneous at **higher** temps ( $T\Delta S > \Delta H$ )
  - ◆ **Exothermic** processes are spontaneous at **lower** temps ( $T\Delta S < \Delta H$ )

## Calculating Entropy of Vaporization

- Phase changes occur at eq:  $\Delta S = \Delta H / T$
- The boiling point of water is 100 °C and the enthalpy change for the conversion of water to steam is  $\Delta H_{\text{vap}} = 40.67$  kJ/mol. What is the entropy change for vaporization,  $\Delta S_{\text{vap}}$ , in J/(K·mol)?
- $\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T$
- $$\Delta S_{\text{vap}} = \frac{40.67 \frac{\text{kJ}}{\text{mol}} \times \frac{1000 \text{J}}{1 \text{kJ}}}{373 \text{K}} = 109 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

## Find T for spontaneous rxn

- Calculate  $\Delta G$  given  $\Delta H = -227$  kJ,  $\Delta S = -309$  J/K,  $T = 1450$  K.

Is this process spontaneous at this temperature? If not, calculate the temperature (in °C) at which this reaction becomes spontaneous. (Hint: set  $\Delta G = 0$  and solve for T!)

## Find T spontaneous rxn

- $\Delta G = +221$  kJ; **not spontaneous**
- $\Delta G = 0$ ;  $\Delta H = T\Delta S$
- $T = \Delta H / \Delta S = -227 \text{ kJ} / -0.309 \text{ kJ/K}$
- $T = 735 \text{ K} = 462 \text{ }^\circ\text{C}$
- **Spontaneous when  $T < 462 \text{ }^\circ\text{C}$**
- (entropy & enthalpy are both -, so it is spontaneous at T below equilibrium T.)

## Standard Free Energy Changes

$\Delta G$  depends on T, P, [ ] and physical states (like  $\Delta H$  and S).

### Standard-state conditions:

- ◆ Solids, liquids, and gases in pure form
- ◆ 1 M Solutions, gases at 1 atm pressure
- ◆ Room temperature: 25°C (298 K)

**Standard free energy change ( $\Delta G^\circ$ )** is the free energy change when reactants in their standard states are converted to products in their standard states.

## Standard Free Energy Changes

1) Can get  $\Delta G^\circ$  from  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

- ◆ Use  $\Delta G^\circ$  to predict spontaneity in the standard state

2)  $\Delta G^\circ$  can also be calculated from standard free energies of formation: ( $\Delta G^\circ_f$ )

$$\Delta G^\circ_{\text{rxn}} = \sum n \Delta G^\circ_f(\text{products}) - \sum n \Delta G^\circ_f(\text{reactants})$$

- ◆  $\Delta G^\circ_f$  = **standard free energy of formation**: the free energy change when **1 mole of a compound** is formed from its **elements in their standard states**.

- ◆  $\Delta G^\circ_f = 0$  for an element in its stable form

- ◆ Values of  $\Delta G^\circ_f$ ,  $\Delta H^\circ_f$ ,  $S^\circ$  are listed in Appendix

## Reaction for $\Delta G^\circ_f$

- Which one of these reactions corresponds to  $\Delta G^\circ_f$  of  $\text{H}_2\text{O}(\text{g})$ ?

- ◆  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- ◆  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
- ◆  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$

## $\Delta G^\circ$ calculation

$\Delta G^\circ_f$ in kJ/mol	
-604.20	CaO(s)
-896.76	Ca(OH) <sub>2</sub> (s)
-228.59	H <sub>2</sub> O(g)
-237.18	H <sub>2</sub> O(l)

$$\Delta G^\circ = \sum n \Delta G^\circ_f(\text{products}) - \sum n \Delta G^\circ_f(\text{reactants})$$

Calculate  $\Delta G^\circ$  for these reactions and predict whether they will be spontaneous.

- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}(\text{OH})_2(\text{s})$
- ❖  $\Delta G^\circ(\text{H}_2\text{O}) = -457.18$  kJ, spontaneous
- ❖  $\Delta G^\circ(\text{Ca}(\text{OH})_2) = -55.38$  kJ, spontaneous

## Relating $\Delta G$ to $\Delta G^\circ$ and Q

**$\Delta G$  is the actual free energy** – this is the free energy change under nonstandard conditions. It changes as a reaction proceeds, as concentrations and/or pressures change.

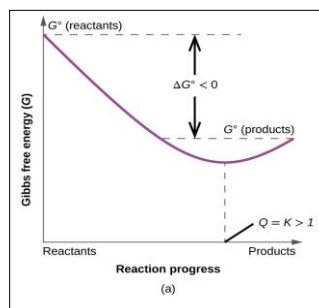
$\Delta G^\circ$  **IS** standard and does **NOT** change during a reaction.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- Q = Reaction Quotient (plug the given [ ]'s and P's into Q)
- R = 8.314 J/mol·K, T in Kelvin

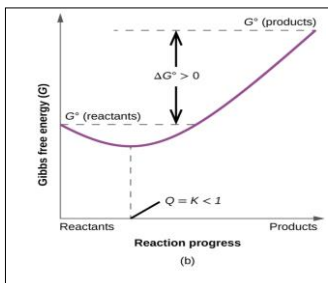
## $\Delta G^\circ$ and Equilibrium

$$\Delta G^\circ < 0 \text{ } (-\Delta G^\circ), \text{ product-favored}$$



## Free Energy Curve for $+\Delta G^\circ$

$\Delta G^\circ > 0$ , Reactant favored



## Free Energy and Equilibrium

$$\Delta G = \Delta G^\circ + RT \ln Q$$

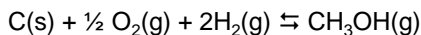
At equilibrium,  $\Delta G = 0$  and  $Q = K$ :

$$\Delta G^\circ = -RT \ln K$$

$\Delta G^\circ$	K	Comment
$\Delta G^\circ < 0$	$K > 1$	Equilibrium mixture contains mostly products.
$\Delta G^\circ > 0$	$K < 1$	Equilibrium mixture contains mostly reactants.
$\Delta G^\circ = 0$	$K = 1$	Equilibrium mixture contains appreciable amount of reactants and products at equilibrium

## Calculating K from $\Delta G^\circ$

$\Delta G^\circ$  is  $-24.7$  kJ/mol for the formation of methanol.



Calculate the equilibrium constant, K, at  $25^\circ\text{C}$  for this reaction.

$$\ln K = -\Delta G^\circ/RT =$$

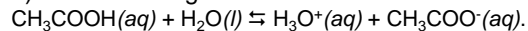
$$-(-24.7 \text{ kJ/mol}) / (0.008314 \text{ kJ/mol}\cdot\text{K} \times 298 \text{ K})$$

$$\ln K = 9.969; K = e^{9.969} = 2.14 \times 10^4$$

## Calculation $\Delta G^\circ$ from K

At  $25^\circ\text{C}$ ,  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .

a) Predict the sign of  $\Delta G^\circ$  for



b) Calculate  $\Delta G^\circ$  at  $25^\circ\text{C}$ .

- $K < 1$  so  $\Delta G^\circ$  is +
- $\Delta G^\circ = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})(\ln 1.8 \times 10^{-5})$
- $\Delta G^\circ = 2.7 \times 10^4 \text{ J/mol}$  (or  $27 \text{ kJ/mol}$ )

## Find $\Delta G$ for weak acid solution

Calculate  $\Delta G$  at  $25^\circ\text{C}$  for the acetic acid equilibrium reaction, when  $[\text{H}_3\text{O}^+] = 0.020 \text{ M}$ ,  $[\text{CH}_3\text{COO}^-] = 0.010 \text{ M}$  and  $[\text{CH}_3\text{COOH}] = 0.10 \text{ M}$ . (Use  $\Delta G^\circ$  from part b.)

$$Q = (0.020)(0.010)/(0.10) = 2.0 \times 10^{-3}$$

$$\Delta G = 27 \text{ kJ/mol} + (0.008314 \text{ kJ/K}\cdot\text{mol})(298 \text{ K})(\ln 0.0020)$$

$\Delta G = 12 \text{ kJ/mol}$  (nonspontaneous in forward direction)  
Note:  $Q > K_a = 1.8 \times 10^{-5}$  so reaction reverses to reach eq.

## Calculate Nonstandard Free Energy

$\Delta G^\circ$  for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$  is  $2.60 \text{ kJ/mol}$  at  $25^\circ\text{C}$ .

In one experiment, the initial pressures are  $P_{\text{H}_2} = 4.3 \text{ atm}$ ,  $P_{\text{I}_2} = 0.34 \text{ atm}$  and  $P_{\text{HI}} = 0.23 \text{ atm}$ .

- Calculate  $\Delta G$  and predict the direction that this reaction will proceed.

$$Q = 0.0362$$

$$\Delta G = 2.60 \text{ kJ/mol} + (8.314 \times 10^{-3} \text{ kJ/K}\cdot\text{mol})(298 \text{ K})(\ln 0.0362)$$

$$\Delta G = -5.6 \text{ kJ/mol}$$

Spontaneous so Eq shifts right

## Calculations Practice

- Calculate  $\Delta G$  for  $S(s) + O_2(g) \rightleftharpoons SO_2(g)$  when  $P_{O_2} = 0.140$  atm and  $P_{SO_2} = 1.24$  atm at  $25^\circ\text{C}$ .
- Need to calculate  $\Delta G^\circ$  and  $Q$ .
  - ◆  $\Delta G^\circ_f(S(s)) = 0$  kJ/mol;  $\Delta G^\circ_f(O_2(g)) = 0$  kJ/mol;  $\Delta G^\circ_f(SO_2(g)) = -300.2$  kJ/mol
- $Q = 1.24 \text{ atm} / 0.140 \text{ atm} = 8.8571$
- $\Delta G^\circ = -300.2$  kJ
- $\Delta G = -295$  kJ