

## Chapter 16

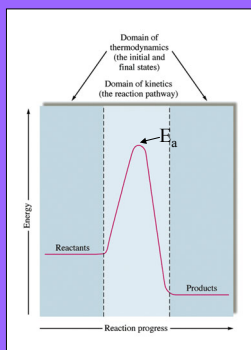
### Spontaneity, Entropy, and Free Energy

## Spontaneous Processes and Entropy

- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.

Figure 16.2:

The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics. Thermodynamics tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.



## First Law of Thermodynamics

- The First Law of Thermodynamics states that the energy of the universe is constant. While energy may change in form (heat, work, etc.) and be exchanged between the system & surroundings - the total energy remains constant. **To describe the system:**
  - Work done by the system is **negative**.
  - Work done on the system is **positive**.
  - Heat evolved by the system is **negative**.
  - Heat absorbed by the system is **positive**.

## Enthalpy and Enthalpy Change

- In Chapter 6, we tentatively defined enthalpy in terms of the relationship of  $\Delta H$  to the **heat at constant pressure**.
- This means that at a given temperature and pressure, a given amount of a substance has a definite enthalpy.
- Therefore, **if you know the enthalpies of substances, you can calculate the change in enthalpy,  $\Delta H$ , for a reaction.**

## Enthalpy and Enthalpy Change

- In Chapter 6, we tentatively defined enthalpy in terms of the relationship of  $\Delta H$  to the **heat at constant pressure**.
  - In practice, we measure certain heats of reactions and use them to tabulate enthalpies of formation,  $\Delta H_f^\circ$ .
  - Standard enthalpies of formation for selected compounds are listed in Appendix 4.

## Enthalpy and Enthalpy Change

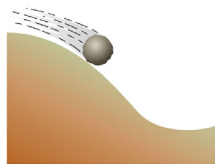
- In Chapter 6, we tentatively defined enthalpy in terms of the relationship of  $\Delta H$  to the **heat at constant pressure**.
- The standard enthalpy change for a reaction is

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

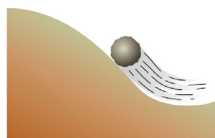
## Spontaneous Processes and Entropy

- A **spontaneous process** is a physical or chemical change that occurs by itself.
  - Examples include:
    - A rock at the top of a hill rolls down.
    - Heat flows from a hot object to a cold one.
    - An iron object rusts in moist air.
- These processes occur without requiring an outside force and **continue until equilibrium is reached**.

Examples of a spontaneous and nonspontaneous process.



Spontaneous process



Nonspontaneous process

## Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** addresses questions about spontaneity in terms of a quantity called **entropy**.
  - Entropy, S**, is a thermodynamic quantity that is a measure of the randomness or disorder or the “available arrangements” for the system or surroundings.
  - The SI unit of entropy is **joules per Kelvin (J/K)** and, like enthalpy, is a state function.

## The Second Law of Thermodynamics

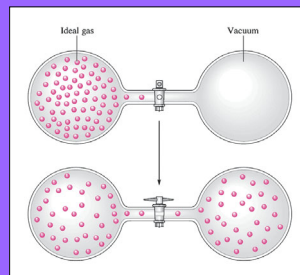
- ... **in any spontaneous process there is always an increase in the entropy of the universe.**

$$\Delta S_{\text{univ}} > 0$$

$$\text{or } \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

- **for a spontaneous process.**

Figure 16.3: The expansion of an ideal gas into an evacuated bulb.



For two molecules, A & B, there are four microstates

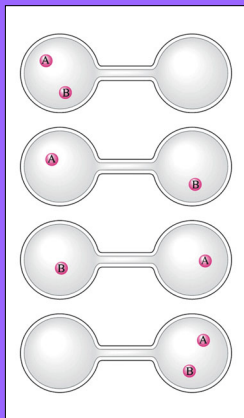


Figure 16.4: Possible arrangements (states) of four molecules in a two-bulbed flask.

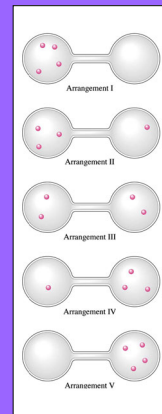


TABLE 16.1 The Microstates That Give a Particular Arrangement (State)

Arrangement	Microstates
I	
II	
III	
IV	
V	

TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
$n$	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
$6 \times 10^{23}$ (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(0.7 \times 10^{24})}$

Nature spontaneously proceeds towards the states that have the highest probabilities of existing.

## Positional Entropy

• A gas expands into a vacuum because the expanded state has the highest **positional probability** of states available to the system.

• Therefore,

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

Solid: Only a few "allowed" positions, molecules or atoms close together

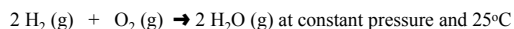
Gas: Many allowed positions, molecules are far apart.

## Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of the universe always increases for a spontaneous process.
- The net change in entropy of the system,  $\Delta S$ , equals the sum of the entropy created during the spontaneous process and the change in energy associated with the heat flow.

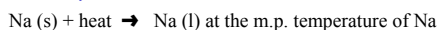
Some examples of entropy changes:

Does entropy of the system increase or decrease for the following?

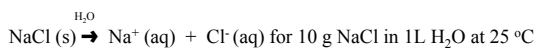


Decreases – simple molecules form more complex molecule,

So  $\Delta S_{\text{system}}$  is -



Increases – atoms of Na have more “available positions” in the liquid state.  $\Delta S_{\text{system}}$  is +



Increases – ions formed from NaCl are more simple in structure and have more available position.  $\Delta S_{\text{system}}$  is +

## Entropy and the Second Law of Thermodynamics

So for any process:  $\Delta S_{\text{universe}} > 0$ , process is spontaneous  
 $\Delta S_{\text{universe}} = 0$ , process tends not to occur, at equilibrium  
 $\Delta S_{\text{universe}} < 0$ , reverse process occurs spontaneously

We can determine  $\Delta S_{\text{system}}$  – How can we determine  $\Delta S_{\text{surroundings}}$ ?

$\Delta S_{\text{surroundings}}$  determined primarily by heat flow between system & surroundings. If heat flows into the surroundings (i.e., when a reaction is exothermic) the random motions of the molecules in the surroundings increase. Thus, the entropy of the surroundings increases.

## Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of the universe always increases for a spontaneous process.
- We can say that for the surroundings

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

## Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of the universe always increases for a spontaneous process.
- At constant T and P,

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

Heat flows into the surroundings during exothermic reactions and out of the surroundings for endothermic reactions

**TABLE 16.3** Interplay of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  in Determining the Sign of  $\Delta S_{\text{univ}}$

Signs of Entropy Changes			
$\Delta S_{\text{sys}}$	$\Delta S_{\text{surr}}$	$\Delta S_{\text{univ}}$	Process Spontaneous?
+	+	+	Yes
-	-	-	No (reaction will occur in opposite direction)
+	-	?	Yes, if $\Delta S_{\text{sys}}$ has a larger magnitude than $\Delta S_{\text{surr}}$
-	+	?	Yes, if $\Delta S_{\text{surr}}$ has a larger magnitude than $\Delta S_{\text{sys}}$

## Entropy and the Second Law of Thermodynamics

The impact of the transfer of a quantity of heat energy to the surroundings will be greater when the temperature is low

- For a given reaction, the sign of  $\Delta S_{\text{surr}}$  depends on whether  $\Delta H_{\text{sys}}$  is + or -. The heat energy transferred to the surroundings will have the opposite sign!
- The magnitude of  $\Delta S_{\text{surr}}$  will depend on the temperature as well as the magnitude of  $\Delta H_{\text{sys}}$ .

## Entropy Change for a Phase Transition

- If during a **phase transition**, such as ice melting, heat is slowly absorbed by the system, it remains near equilibrium as the ice melts.
  - Under these conditions, no significant amount of entropy is created.
  - The entropy results entirely from the absorption of heat. Therefore,

$$\Delta S = \frac{q}{T} \quad (\text{For an equilibrium process})$$

## Entropy Change for a Phase Transition

- If during a **phase transition**, such as ice melting, heat is slowly absorbed by the system, it remains near equilibrium as the ice melts.
  - Other phase changes, such as vaporization of a liquid, also occur under equilibrium conditions.
  - Therefore, you can use the previous equation to obtain the  $\Delta S_{\text{sys}}$  for a phase change. For the melting of 1 mole of ice at 0°C, the  $\Delta S_{\text{sys}}$  is

$$\Delta S_{\text{sys}} = +6.03 \text{ kJ}/273 \text{ K} = +0.0221 \text{ kJ}/(\text{mole} \cdot \text{K})$$

## A Problem To Consider

- The heat of vaporization,  $\Delta H_{\text{vap}}$  of carbon tetrachloride,  $\text{CCl}_4$ , at 25 °C is 43.0 kJ/mol. If 1 mol of liquid  $\text{CCl}_4$  has an entropy of 214 J/K, what is the entropy of 1 mol of the vapor at this temperature?
  - When liquid  $\text{CCl}_4$  evaporates, it absorbs heat:  $\Delta H_{\text{vap}} = 43.0 \text{ kJ/mol}$  ( $43.0 \times 10^3 \text{ J/mol}$ ) at 25 °C, or 298 K. The entropy change,  $\Delta S$ , is

$$\Delta S_{\text{sys}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{43.0 \times 10^3 \text{ J/mol}}{298 \text{ K}} = 144 \text{ J}/(\text{mol} \cdot \text{K})$$

## A Problem To Consider

- The heat of vaporization,  $\Delta H_{\text{vap}}$  of carbon tetrachloride,  $\text{CCl}_4$ , at 25 °C is 43.0 kJ/mol. If 1 mol of liquid  $\text{CCl}_4$  has an entropy of 214 J/K, what is the entropy of 1 mol of the vapor at this temperature?
  - In other words, 1 mol of  $\text{CCl}_4$  increases in entropy by 144 J/K when it vaporizes.
    - The entropy of 1 mol of vapor equals the entropy of 1 mol of liquid (214 J/K) plus 144 J/K.

$$S_{\text{vap}} = \text{Entropy of vapor} = (214 + 144) \text{ J/K} = 358 \text{ J}/(\text{mol} \cdot \text{K})$$

Since  $\Delta S_{\text{sys}} = S_{\text{vap}} - S_{\text{liq}}$

## Standard Entropies and the Third Law of Thermodynamics

- The **third law of thermodynamics** states that a substance that is perfectly crystalline at 0 K has an entropy of zero.
  - When temperature is raised, however, the substance becomes more disordered as it absorbs heat.
  - The entropy of a substance is determined by measuring how much heat is required to change its temperature per Kelvin degree.

Figure 16.5: (a) A perfect crystal of hydrogen chloride at 0 K. (b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy.

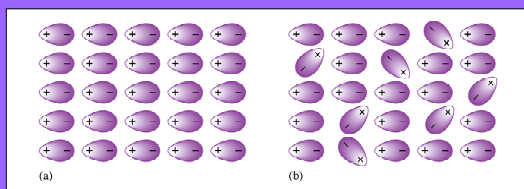
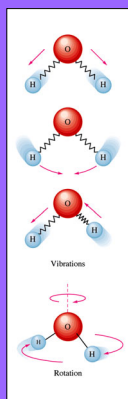
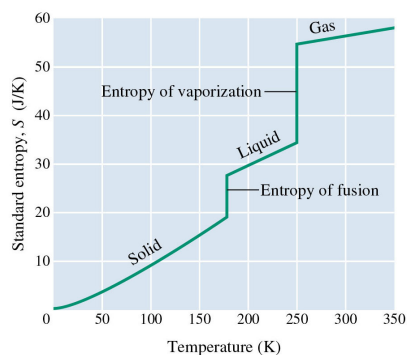


Figure 16.6: The H<sub>2</sub>O molecule can vibrate and rotate in several ways, some of which are shown here.



Standard entropy of methyl chloride, CH<sub>3</sub>Cl, at various temperatures.



## Standard Entropies and the Third Law of Thermodynamics

- The **standard entropy** of a substance or ion (Appendix 4), also called its **absolute entropy, S°**, is the entropy value for the standard state of the species.
- Standard state implies 25 °C, 1 atm pressure, and 1 M for dissolved substances.

Table 19.1  
Standard Entropies (at 25 °C)

Formula	S°, J/(mol · K)	Formula	S°, J/(mol · K)	Formula	S°, J/(mol · K)
<b>Hydrogen</b>					
H <sub>2</sub> (g)	0	CS <sub>2</sub> (l)	151.0	Sulfur	
H <sub>2</sub> (g)	130.6	HClN(g)	201.7	S <sub>2</sub> (g)	228.1
<b>Sodium</b>					
Na <sup>+</sup> (aq)	60.2	CCl <sub>4</sub> (g)	309.7	Si(monoclinic)	32.6
Na(s)	51.4	CCl <sub>4</sub> (l)	214.4	Si(s)	248.1
NaCl(s)	72.1	CH <sub>3</sub> CHO(g)	266	H <sub>2</sub> S(g)	205.6
<b>Calcium</b>					
NaHCO <sub>3</sub> (s)	102	C <sub>2</sub> H <sub>5</sub> OH(l)	161	Fluorine	
Na <sub>2</sub> CO <sub>3</sub> (s)	139	Si(s)	18.0	F <sup>-</sup> (aq)	-9.6
Ca <sup>2+</sup> (aq)	-55.2	SiO <sub>2</sub> (s)	41.5	HF(g)	173.7
Ca(s)	41.6	SiF <sub>4</sub> (g)	285	Chlorine	
CaO(s)	38.2	Pb(s)	64.8	Cl <sup>-</sup> (aq)	55.1
CaCO <sub>3</sub> (s)	92.9	PbO(s)	66.5	Cl <sub>2</sub> (g)	223.0
<b>Carbon</b>					
C(graphite)	5.7	Pb(s)	91.3	HCl(g)	186.8
C(diamond)	2.4	Nitrogen		Bromine	
CO(g)	197.5	N <sub>2</sub> (g)	191.5	Br <sup>-</sup> (aq)	80.7
CO <sub>2</sub> (g)	213.7	NH <sub>3</sub> (g)	193	Br <sub>2</sub> (l)	152.2
HCO <sub>3</sub> <sup>-</sup> (aq)	95.0	NO(g)	210.6	Iodine	
CH <sub>4</sub> (g)	186.1	NO <sub>2</sub> (g)	239.9	I <sup>-</sup> (aq)	109.4
C <sub>2</sub> H <sub>6</sub> (g)	219.2	HNO <sub>3</sub> (aq)	146	I <sub>2</sub> (s)	116.1
C <sub>3</sub> H <sub>8</sub> (g)	229.5	Oxygen		Silver	
C <sub>4</sub> H <sub>10</sub> (l)	172.8	O <sub>2</sub> (g)	205.0	Ag <sup>+</sup> (aq)	73.9
HCHO(g)	219	O <sub>3</sub> (g)	238.8	Ag(s)	42.7
CH <sub>3</sub> OH(l)	127	OH <sup>-</sup> (aq)	-10.5	AgBr(s)	84
CS <sub>2</sub> (g)	237.8	H <sub>2</sub> O(g)	188.7	AgBr(s)	96.1
		H <sub>2</sub> O(l)	69.9	AgI(s)	107.1
				AgI(s)	114

\*See Appendix C for additional values.

## Standard Entropies and the Third Law of Thermodynamics

- The **standard entropy** of a substance or ion (Table 19.1), also called its **absolute entropy, S°**, is the entropy value for the standard state of the species.
- Note that the **elements have nonzero values**, unlike standard enthalpies of formation, ΔH<sub>f</sub><sup>°</sup>, which by convention, are zero.

## Standard Entropies and the Third Law of Thermodynamics

- The **standard entropy** of a substance or ion (Appendix 4), also called its **absolute entropy, S°**, is the entropy value for the standard state of the species.
- The symbol S°, rather than ΔS°, is used for standard entropies to emphasize that they originate from the third law.

## Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained  $\Delta H^\circ$ .

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

- Even without knowing the values for the entropies of substances, you can sometimes predict the sign of  $\Delta S^\circ$  for a reaction.

## Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained  $\Delta H^\circ$ .
  - The entropy usually increases in the following situations:
    - A reaction in which a molecule is broken into two or more smaller molecules.

## Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained  $\Delta H^\circ$ .
  - The entropy usually increases in the following situations:
    - A reaction in which there is an increase in the moles of gases.

## Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained  $\Delta H^\circ$ .
  - The entropy usually increases in the following situations:
    - A process in which a solid changes to liquid or gas or a liquid changes to gas.

## A Problem To Consider

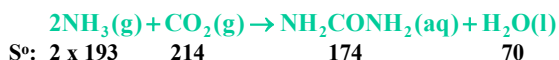
- Calculate the change in entropy,  $\Delta S^\circ$ , at 25 °C for the reaction in which urea is formed from  $\text{NH}_3$  and  $\text{CO}_2$ . The standard entropy of  $\text{NH}_2\text{CONH}_2$  is 174 J/(mol·K). See Appendix 4 for other values.



- The calculation is similar to that used to obtain  $\Delta H^\circ$  from standard enthalpies of formation.

## A Problem To Consider

- Calculate the change in entropy,  $\Delta S^\circ$ , at 25 °C for the reaction in which urea is formed from  $\text{NH}_3$  and  $\text{CO}_2$ . The standard entropy of  $\text{NH}_2\text{CONH}_2$  is 174 J/(mol·K). See Appendix 4 for other values.



- It is convenient to put the standard entropies (multiplied by their stoichiometric coefficients) below the formulas.

## A Problem To Consider

- Calculate the change in entropy,  $\Delta S^\circ$ , at 25 °C for the reaction in which urea is formed from  $\text{NH}_3$  and  $\text{CO}_2$ . The standard entropy of  $\text{NH}_2\text{CONH}_2$  is 174 J/(mol·K). See Appendix 4 for other values.



- We can now use the summation law to calculate the entropy change.

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

## A Problem To Consider

- Calculate the change in entropy,  $\Delta S^\circ$ , at 25 °C for the reaction in which urea is formed from  $\text{NH}_3$  and  $\text{CO}_2$ . The standard entropy of  $\text{NH}_2\text{CONH}_2$  is 174 J/(mol·K). See Appendix 4 for other values.



- We can now use the summation law to calculate the entropy change.

$$\Delta S^\circ = [(174 + 70) - (2 \times 193 + 214)] \text{ J/K} = -356 \text{ J/K}$$

TABLE 16.4 Results of the Calculation of  $\Delta S_{\text{sys}}$  and  $\Delta G^\circ$  for the Process  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$  at -10°C, 0°C, and 10°C

T (°C)	T (K)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/K·mol)	$\Delta S_{\text{surr}} = \frac{\Delta H^\circ}{T}$ (J/K·mol)	$\Delta S_{\text{sys}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K·mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	$6.03 \times 10^3$	22.1	-22.9	-0.8	$5.81 \times 10^3$	$+2.2 \times 10^2$
0	273	$6.03 \times 10^3$	22.1	-21.4	0	$6.03 \times 10^3$	0
10	283	$6.03 \times 10^3$	22.1	-21.4	+0.8	$6.23 \times 10^3$	$-2.2 \times 10^2$

$$\Delta S_{\text{sys}} = (6.03 \times 10^3 \text{ J}/273 \text{ K})$$

At -10°C,  $\Delta S_{\text{surr}}$  is negative and larger than  $\Delta S_{\text{sys}}$ , so  $\Delta S_{\text{univ}}$  is negative and reverse process is spontaneous

At 0 °C,  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ , so process is at equilibrium

At 10 °C,  $\Delta S_{\text{sys}}$  is + and  $> \Delta S_{\text{surr}}$ , so  $\Delta S_{\text{univ}}$  is + and the process is spontaneous

## Free Energy Concept

- The American physicist J. Willard Gibbs introduced the concept of **free energy** (sometimes called the **Gibbs free energy**), **G**, which is a thermodynamic quantity defined by the equation  **$G = H - TS$** , or for processes undergoing change:  **$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$** .
  - This quantity gives a direct criterion for spontaneity of reaction.

$$\text{Since } \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

Dividing by -T

$$-\Delta G/T = -\Delta H_{\text{sys}}/T + \Delta S_{\text{sys}}$$

But  $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$  so that

$$-\Delta G/T = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}, \text{ but } \Delta S_{\text{universe}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}$$

-Therefore, when  $\Delta G$  is negative,

$\Delta S_{\text{univ}}$  is + and process is spontaneous

These equations apply to processes occurring at constant T & P, and in which no useful work is done!

## Free Energy and Spontaneity

- Changes in **H** and **S** during a reaction result in a **change in free energy,  $\Delta G$** , given by the equation

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

- Thus, if you can show that  **$\Delta G$  is negative** at a given temperature and pressure, you can predict that **the reaction will be spontaneous**.
- If  **$\Delta G = 0$** , the reaction is at **equilibrium**
- If  **$\Delta G$  is positive**, the reaction is **nonspontaneous**



## Effect of $\Delta H$ and $\Delta S$ on Spontaneity

$\Delta H$	$\Delta S$	Result
-	+	spontaneous at all temps
+	+	spontaneous at high temps
-	-	spontaneous at low temps
+	-	not spontaneous at <u>any</u> temp

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

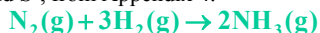
## Standard Free-Energy Change

- The **standard free energy change,  $\Delta G^\circ$** , is the free energy change that occurs when reactants and products are in their standard states.
- The next example illustrates the calculation of the standard free energy change,  $\Delta G^\circ$ , from  $\Delta H^\circ$  and  $\Delta S^\circ$ .

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

## A Problem To Consider

- What is the standard free energy change,  $\Delta G^\circ$ , for the following reaction at 25 °C? Use values of  $\Delta H_f^\circ$  and  $S^\circ$ , from Appendix 4.



$$\Delta H_f^\circ: \quad 0 \quad \quad 0 \quad \quad 2 \times (-45.9) \text{ kJ}$$

$$S^\circ: \quad 191.5 \quad 3 \times 130.6 \quad 2 \times 193 \text{ J/K}$$

- Place below each formula the values of  $\Delta H_f^\circ$  and  $S^\circ$  multiplied by stoichiometric coefficients.

## A Problem To Consider

- What is the standard free energy change,  $\Delta G^\circ$ , for the following reaction at 25 °C? Use values of  $\Delta H_f^\circ$  and  $S^\circ$ , from Appendix 4.

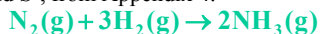


- You can calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  using their respective summation laws.

$$\begin{aligned} \Delta H^\circ &= \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants}) \\ &= [2 \times (-45.9) - 0] \text{ kJ} = -91.8 \text{ kJ} \end{aligned}$$

## A Problem To Consider

- What is the standard free energy change,  $\Delta G^\circ$ , for the following reaction at 25 °C? Use values of  $\Delta H_f^\circ$  and  $S^\circ$ , from Appendix 4.

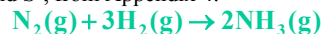


- You can calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  using their respective summation laws.

$$\begin{aligned} \Delta S^\circ &= \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants}) \\ &= [2 \times 193 - (191.5 + 3 \times 130.6)] \text{ J/K} = -197 \text{ J/K} \end{aligned}$$

## A Problem To Consider

- What is the standard free energy change,  $\Delta G^\circ$ , for the following reaction at 25 °C? Use values of  $\Delta H_f^\circ$  and  $S^\circ$ , from Appendix 4.



- Now substitute into our equation for  $\Delta G^\circ$ . Note that  $\Delta S^\circ$  is converted to kJ/K.

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -91.8 \text{ kJ} - (298 \text{ K})(-0.197 \text{ kJ/K}) \\ &= -33.1 \text{ kJ} \end{aligned}$$

## Standard Free Energies of Formation

- The **standard free energy of formation,  $\Delta G_f^\circ$** , of a substance is the free energy change that occurs when 1 mol of a substance is formed from its elements in their stablest states at 1 atm pressure and 25 °C.
- By tabulating  $\Delta G_f^\circ$  for substances, as in Appendix 4, **you can calculate the  $\Delta G^\circ$**  for a reaction by using a summation law.

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

Table 19.2  
Standard Free Energies of Formation (at 25 °C)

Formula	$\Delta G_f^\circ$ , kJ/mol*	Formula	$\Delta G_f^\circ$ , kJ/mol	Formula	$\Delta G_f^\circ$ , kJ/mol
<b>Hydrogen</b>					
H <sub>2</sub> O (aq)	0	CS <sub>2</sub> (l)	63.6	S <sub>2</sub> (g)	80.1
H <sub>2</sub> (g)	0	HCN(g)	125	S(rhombic)	0
<b>Sodium</b>					
Na (aq)	-261.9	CCl <sub>4</sub> (g)	-53.7	SO <sub>2</sub> (g)	-300.2
Na(s)	0	CCl <sub>4</sub> (l)	-68.6	H <sub>2</sub> S(g)	-33
NaCl(s)	-384.0	CH <sub>3</sub> CHO(g)	-133.7	<b>Fluorine</b>	
NaHCO <sub>3</sub> (s)	-819.1	C <sub>2</sub> H <sub>5</sub> OH(l)	-174.8	F (aq)	-276.5
Na <sub>2</sub> CO <sub>3</sub> (s)	-1048.1	<b>Silicon</b>		Si(g)	0
<b>Calcium</b>					
Ca <sup>2+</sup> (aq)	-553.0	SiO <sub>2</sub> (s)	-856.5	Cl <sub>2</sub> (g)	-275
Ca(s)	0	SiF <sub>4</sub> (g)	-1506	F (aq)	-131.2
CaBr(s)	-603.5	<b>Lead</b>		Cl <sub>2</sub> (g)	0
CaCO <sub>3</sub> (s)	-1128.8	Pb(s)	0	HCl(g)	-95.3
<b>Carbon</b>					
C(graphite)	0	PbO(s)	-189.2	<b>Bromine</b>	
C(diamond)	2.9	PbS(s)	-96.7	Br (aq)	-102.8
CO(g)	-137.2	N <sub>2</sub> (g)	0	Br <sub>2</sub> (l)	0
CO <sub>2</sub> (g)	-394.4	NH <sub>3</sub> (g)	-16	I (aq)	-51.7
HCO <sub>3</sub> <sup>-</sup> (aq)	-587.1	NO <sub>2</sub> (g)	86.60	I <sub>2</sub> (s)	0
CH <sub>4</sub> (g)	-50.8	NO(g)	51	<b>Silver</b>	
C <sub>2</sub> H <sub>4</sub> (g)	68.4	HNO <sub>2</sub> (aq)	-110.5	Ag (aq)	77.1
C <sub>2</sub> H <sub>6</sub> (g)	-32.9	<b>Oxygen</b>		Ag(s)	0
C <sub>2</sub> H <sub>5</sub> (l)	124.5	O <sub>2</sub> (g)	0	AgBr(s)	-185
HCHO(g)	-110	O <sub>3</sub> (g)	163	AgCl(s)	-109.7
CH <sub>3</sub> OH(l)	-166.2	OH <sup>-</sup> (aq)	-157.3	AgBr(s)	-95.9
CS <sub>2</sub> (g)	66.9	H <sub>2</sub> O(g)	-228.6	AgI(s)	-66.3
		H <sub>2</sub> O(l)	-237.2		

\*See Appendix C for additional values.

## A Problem To Consider

- Calculate  $\Delta G^\circ$  for the combustion of 1 mol of ethanol, C<sub>2</sub>H<sub>5</sub>OH, at 25 °C. Use the standard free energies of formation given in Appendix 4.



$$\Delta G_f^\circ: \quad -174.8 \quad 0 \quad 2(-394.4) \quad 3(-228.6)\text{kJ}$$

- Place below each formula the values of  $\Delta G_f^\circ$  multiplied by stoichiometric coefficients.

## A Problem To Consider

- Calculate  $\Delta G^\circ$  for the combustion of 1 mol of ethanol, C<sub>2</sub>H<sub>5</sub>OH, at 25 °C. Use the standard free energies of formation given in Appendix 4.



$$\Delta G_f^\circ: \quad -174.8 \quad 0 \quad 2(-394.4) \quad 3(-228.6)\text{kJ}$$

- You can calculate  $\Delta G^\circ$  using the summation law.

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

$$\Delta G^\circ = [2(-394.4) + 3(-228.6) - (-174.8)] \text{kJ}$$

## A Problem To Consider

- Calculate  $\Delta G^\circ$  for the combustion of 1 mol of ethanol, C<sub>2</sub>H<sub>5</sub>OH, at 25 °C. Use the standard free energies of formation given in Appendix 4.



$$\Delta G_f^\circ: \quad -174.8 \quad 0 \quad 2(-394.4) \quad 3(-228.6)\text{kJ}$$

- You can calculate  $\Delta G^\circ$  using the summation law.

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

$$\Delta G^\circ = -1299.8 \text{ kJ}$$

## $\Delta G^\circ$ as a Criteria for Spontaneity

- The following rules are useful in judging the spontaneity of a reaction.
  - When  $\Delta G^\circ$  is a large negative number (more negative than about -10 kJ), **the reaction is spontaneous as written**, and the reactants transform almost entirely to products when equilibrium is reached.

## $\Delta G^\circ$ as a Criteria for Spontaneity

- The following rules are useful in judging the spontaneity of a reaction.
  - When  $\Delta G^\circ$  is a large positive number (more positive than about +10 kJ), **the reaction is nonspontaneous as written**, and reactants do not give significant amounts of product at equilibrium.

## $\Delta G^\circ$ as a Criteria for Spontaneity

- The following rules are useful in judging the spontaneity of a reaction.
  - When  $\Delta G^\circ$  is a small negative or positive value (less than about 10 kJ), the reaction gives **an equilibrium mixture with significant amounts of both reactants and products**.

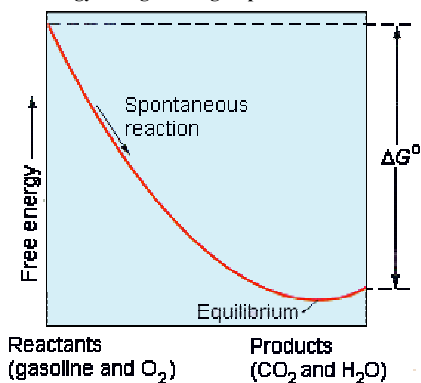
**TABLE 16.5** Various Possible Combinations of  $\Delta H$  and  $\Delta S$  for a Process and the Resulting Dependence of Spontaneity on Temperature

Case	Result
$\Delta S$ positive, $\Delta H$ negative	Spontaneous at all temperatures
$\Delta S$ positive, $\Delta H$ positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
$\Delta S$ negative, $\Delta H$ negative	Spontaneous at low temperatures (where exothermicity is dominant)
$\Delta S$ negative, $\Delta H$ positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

## Free Energy Change During Reaction

- As a system approaches equilibrium, the **instantaneous change in free energy approaches zero**.
  - The next figure illustrates the change in free energy during a spontaneous reaction.
  - As the reaction proceeds, the free energy eventually reaches its minimum value.
  - At that point,  $\Delta G = 0$ , and the net reaction stops; it comes to **equilibrium**.

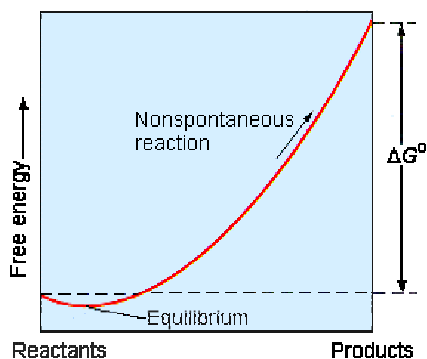
Free-energy change during a spontaneous reaction.



## Free Energy Change During Reaction

- As a system approaches equilibrium, the **instantaneous change in free energy approaches zero**.
  - The next figure illustrates the change in free energy during a **nonspontaneous** reaction.
  - Note that there is a small decrease in free energy as the system goes to equilibrium.

Free-energy change during a nonspontaneous reaction.



## Relating $\Delta G^\circ$ to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change,  $\Delta G^\circ$ , by the following equation.

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

- Here  $Q$  is the thermodynamic form of the reaction quotient.

## Relating $\Delta G^\circ$ to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change,  $\Delta G^\circ$ , by the following equation.

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

- $\Delta G$  represents an instantaneous change in free energy at some point in the reaction approaching equilibrium.

## Relating $\Delta G^\circ$ to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change,  $\Delta G^\circ$ , by the following equation.

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

- At equilibrium,  $\Delta G=0$  and the reaction quotient  $Q$  becomes the equilibrium constant  $K$ .

## Relating $\Delta G^\circ$ to the Equilibrium Constant

- The free energy change when reactants are **in non-standard states** (other than 1 atm pressure or 1 M) is related to the standard free energy change,  $\Delta G^\circ$ , by the following equation.

$$0 = \Delta G^\circ + RT \ln K$$

- At equilibrium,  $\Delta G=0$  and the reaction quotient  $Q$  becomes the equilibrium constant  $K$ .

## Relating $\Delta G^\circ$ to the Equilibrium Constant

- This result easily rearranges to give the basic equation **relating the standard free-energy change to the equilibrium constant**.

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

- When  $K > 1$ , the  $\ln K$  is positive and  $\Delta G^\circ$  is negative.
- When  $K < 1$ , the  $\ln K$  is negative and  $\Delta G^\circ$  is positive.

**TABLE 16.6**

**Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction**

$\Delta G^\circ$	$K$
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

## A Problem To Consider

- Find the value for the equilibrium constant,  $K$ , at 25 °C (298 K) for the following reaction. The standard free-energy change,  $\Delta G^\circ$ , at 25 °C equals  $-13.6$  kJ.



- Rearrange the equation  $\Delta G^\circ = -RT \ln K$  to give

$$\ln K = \frac{\Delta G^\circ}{-RT}$$

## A Problem To Consider

- Find the value for the equilibrium constant,  $K$ , at 25 °C (298 K) for the following reaction. The standard free-energy change,  $\Delta G^\circ$ , at 25 °C equals  $-13.6$  kJ.



- Substituting numerical values into the equation,

$$\ln K = \frac{-13.6 \times 10^3 \text{ J}}{-8.31 \text{ J}/(\text{mol} \cdot \text{K}) \times 298 \text{ K}} = 5.49$$

## A Problem To Consider

- Find the value for the equilibrium constant,  $K$ , at 25 °C (298 K) for the following reaction. The standard free-energy change,  $\Delta G^\circ$ , at 25 °C equals  $-13.6$  kJ.



- Hence,

$$K = e^{5.49} = 2.42 \times 10^2$$

## Calculation of $\Delta G^\circ$ at Various Temperatures

- In this method you assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  are essentially constant with respect to temperature.
- You get the value of  $\Delta G_T^\circ$  at any temperature  $T$  by substituting values of  $\Delta H^\circ$  and  $\Delta S^\circ$  at 25 °C into the following equation.

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

**Table 19.3**  
Effect of Temperature on the Spontaneity of Reactions

$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	Description*	Example
-	+	-	Spontaneous at all $T$	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \longrightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$
+	-	+	Nonspontaneous at all $T$	$3\text{O}_2(\text{g}) \longrightarrow 2\text{O}_3(\text{g})$
-	-	+ or -	Spontaneous at low $T$ ; nonspontaneous at high $T$	$2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) \longrightarrow \text{NH}_2\text{CONH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
+	+	+ or -	Nonspontaneous at low $T$ ; spontaneous at high $T$	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s}) + 2\text{NH}_4\text{NO}_3(\text{s}) \longrightarrow \text{Ba}(\text{NO}_3)_2(\text{aq}) + 2\text{NH}_3(\text{g}) + 10\text{H}_2\text{O}(\text{l})$

\*The terms low temperature and high temperature are relative. For a particular reaction, high temperature could mean room temperature.

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$$\begin{array}{l} \Delta H_f^\circ: \quad -1206.9 \qquad -635.1 \qquad -393.5 \text{ kJ} \\ S^\circ: \quad 92.9 \qquad 38.2 \qquad 213.7 \text{ J/K} \end{array}$$

- Place below each formula the values of  $\Delta H_f^\circ$  and  $S^\circ$  multiplied by stoichiometric coefficients.

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$$\begin{array}{l} \Delta H_f^\circ: \quad -1206.9 \qquad -635.1 \qquad -393.5 \text{ kJ} \\ S^\circ: \quad 92.9 \qquad 38.2 \qquad 213.7 \text{ J/K} \end{array}$$

- You can calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  using their respective summation laws.

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$$\begin{array}{l} \Delta H_f^\circ: \quad -1206.9 \qquad -635.1 \qquad -393.5 \text{ kJ} \\ S^\circ: \quad 92.9 \qquad 38.2 \qquad 213.7 \text{ J/K} \end{array}$$

$$\begin{aligned} \Delta H^\circ &= \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants}) \\ &= [(-635.1 - 393.5) - (-1206.9)]\text{kJ} = 178.3 \text{ kJ} \end{aligned}$$

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$$\begin{array}{l} \Delta H_f^\circ: \quad -1206.9 \qquad -635.1 \qquad -393.5 \text{ kJ} \\ S^\circ: \quad 92.9 \qquad 38.2 \qquad 213.7 \text{ J/K} \end{array}$$

$$\begin{aligned} \Delta S^\circ &= \sum n\Delta S^\circ(\text{products}) - \sum m\Delta S^\circ(\text{reactants}) \\ &= [(38.2 + 213.7) - (92.9)] = 159.0 \text{ J/K} \end{aligned}$$

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$$\begin{array}{l} \Delta H_f^\circ: \quad -1206.9 \qquad -635.1 \qquad -393.5 \text{ kJ} \\ S^\circ: \quad 92.9 \qquad 38.2 \qquad 213.7 \text{ J/K} \end{array}$$

- Now you substitute  $\Delta H^\circ$ ,  $\Delta S^\circ$  (=0.1590 kJ/K), and T (=298K) into the equation for  $\Delta G_f^\circ$ .

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

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$$\begin{array}{l} \Delta H_f^\circ: \quad -1206.9 \qquad -635.1 \qquad -393.5 \text{ kJ} \\ S^\circ: \quad 92.9 \qquad 38.2 \qquad 213.7 \text{ J/K} \end{array}$$

- Now you substitute  $\Delta H^\circ$ ,  $\Delta S^\circ$  (=0.1590 kJ/K), and T (=298K) into the equation for  $\Delta G_f^\circ$ .

$$\Delta G_T^\circ = 178.3\text{kJ} - (298 \text{ K})(0.1590 \text{ kJ/K})$$

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$\Delta H_f^\circ$ :	-1206.9	-635.1	-393.5 kJ
$S^\circ$ :	92.9	38.2	213.7 J/K

- Now you substitute  $\Delta H^\circ$ ,  $\Delta S^\circ$  (=0.1590 kJ/K), and T (=298K) into the equation for  $\Delta G_f^\circ$ .

$$\Delta G_T^\circ = 130.9 \text{ kJ}$$

So the reaction is  
**nonspontaneous**  
at 25 °C.

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$\Delta H_f^\circ$ :	-1206.9	-635.1	-393.5 kJ
$S^\circ$ :	92.9	38.2	213.7 J/K

- Now we'll use 1000 °C (1273 K) along with our previous values for  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta G_T^\circ = 178.3 \text{ kJ} - (1273 \text{ K})(0.1590 \text{ kJ/K})$$

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$\Delta H_f^\circ$ :	-1206.9	-635.1	-393.5 kJ
$S^\circ$ :	92.9	38.2	213.7 J/K

- Now we'll use 1000 °C (1273 K) along with our previous values for  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta G_T^\circ = -24.1 \text{ kJ}$$

So the reaction is  
**spontaneous** at  
1000 °C.

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$\Delta H_f^\circ$ :	-1206.9	-635.1	-393.5 kJ
$S^\circ$ :	92.9	38.2	213.7 J/K

- To determine the minimum temperature for spontaneity, we can set  $\Delta G_f^\circ = 0$  and solve for T.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$\Delta H_f^\circ$ :	-1206.9	-635.1	-393.5 kJ
$S^\circ$ :	92.9	38.2	213.7 J/K

- To determine the minimum temperature for spontaneity, we can set  $\Delta G_f^\circ = 0$  and solve for T.

$$T = \frac{178.3 \text{ kJ}}{0.1590 \text{ kJ/K}} = 1121 \text{ K (848 } ^\circ\text{C)}$$

## A Problem To Consider

- Find the  $\Delta G^\circ$  for the following reaction at 25 °C and 1000 °C. Relate this to reaction spontaneity.



$\Delta H_f^\circ$ :	-1206.9	-635.1	-393.5 kJ
$S^\circ$ :	92.9	38.2	213.7 J/K

- Thus,  $\text{CaCO}_3$  should be thermally stable until its heated to approximately 848 °C.

## Temperature Dependence of K

$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T \Delta S^\circ$  and dividing both sides by T & R,  
multiply both sides by -1

$$\ln(K) = -\frac{\Delta H^\circ}{R} \left(1/T\right) + \Delta S^\circ/R$$

•  $y = mx + b$

• ( $\Delta H^\circ$  and  $S^\circ \approx$  independent of temperature over a small temperature range)

## Maximum Work

- Often reactions are not carried out in a way that does useful **work**.
- As a spontaneous precipitation reaction occurs, the free energy of the system decreases and entropy is produced, but **no useful work is obtained**.
- In principle, if a reaction is carried out to obtain the maximum useful work, no entropy is produced.

## Maximum Work

- Often reactions are not carried out in a way that does useful **work**.
- It can be shown that the maximum useful work,  $w_{\max}$ , for a spontaneous reaction is  $\Delta G$ .

$$w_{\max} = \Delta G$$

- The term **free energy** comes from this result.

## Reversible v. Irreversible Processes

- **Reversible:** The universe is **exactly the same** as it was before the cyclic process.
- **Irreversible:** The universe is **different** after the cyclic process.
- **All real processes are irreversible** -- (some work is changed to heat).

Figure 16.10: A battery can do work by sending current to a starter motor.

