CHEMICAL THERMODYNAMICS

- Spontaneous reactions
- Nonspontaneous reactions
- Enthalpy change (ΔH)
- Exothermic and endothermic reactions
- Entropy change (ΔS)
- Gibbs free energy change, (ΔG)
- Free energy of formation

CHEMICAL THERMODYNAMICS

Fundamental Law of Nature

Any chemical system will tend to undergo an irreversible change from some initial, nonequilibrium state to a final, equilibrium state.

$$aA + bB \leftrightarrow cC + dD$$

At equilibrium, the total energy of the system is minimum.

What Makes a Reaction Spontaneous ?

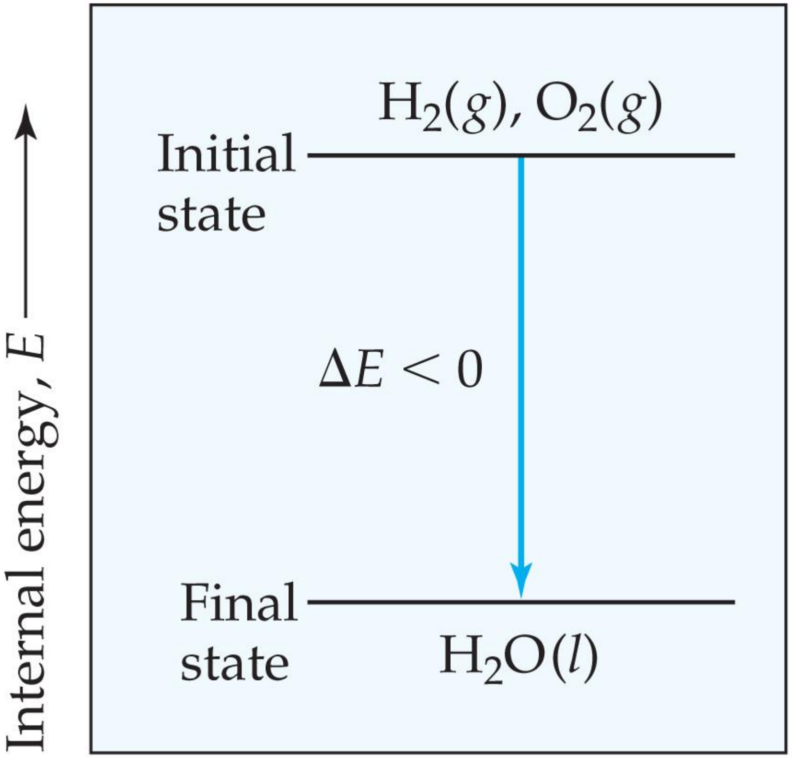
Chemical change and energy are always related.

When the reactant material contains large amounts of energy relative to the products, the chemical reaction occurs spontaneously.

$$aA + bB \leftrightarrow cC + dD$$

(A and B have more energy than C and D. Therefore, reaction can occur spontaneously.)

Thus, a spontaneous chemical reaction is a process in which matter moves toward a more stable state.



E_{initial} greater than E_{final}, energy released from system to surroundings during reaction, $\Delta E < 0$

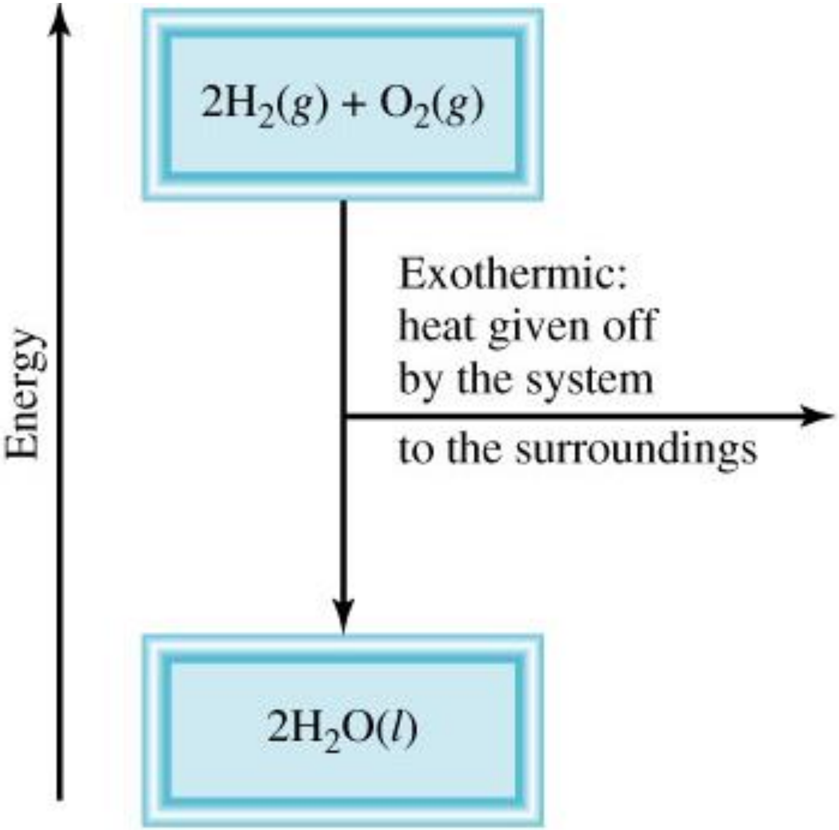
Enthalpy change (ΔH)

A chemical reaction that releases heat (that is, for which ΔH is negative) is an ***exothermic reaction***.

A chemical reaction that takes up heat (that is, for which ΔH is positive) is an ***endothermic reaction***.

When a chemical reaction releases large amounts of heat (has a large negative enthalpy change), it is said to be ***strongly exothermic.***

When a chemical reaction absorbs large amounts of heat (has a large positive enthalpy change), it is said to be ***strongly endothermic.***



Energy

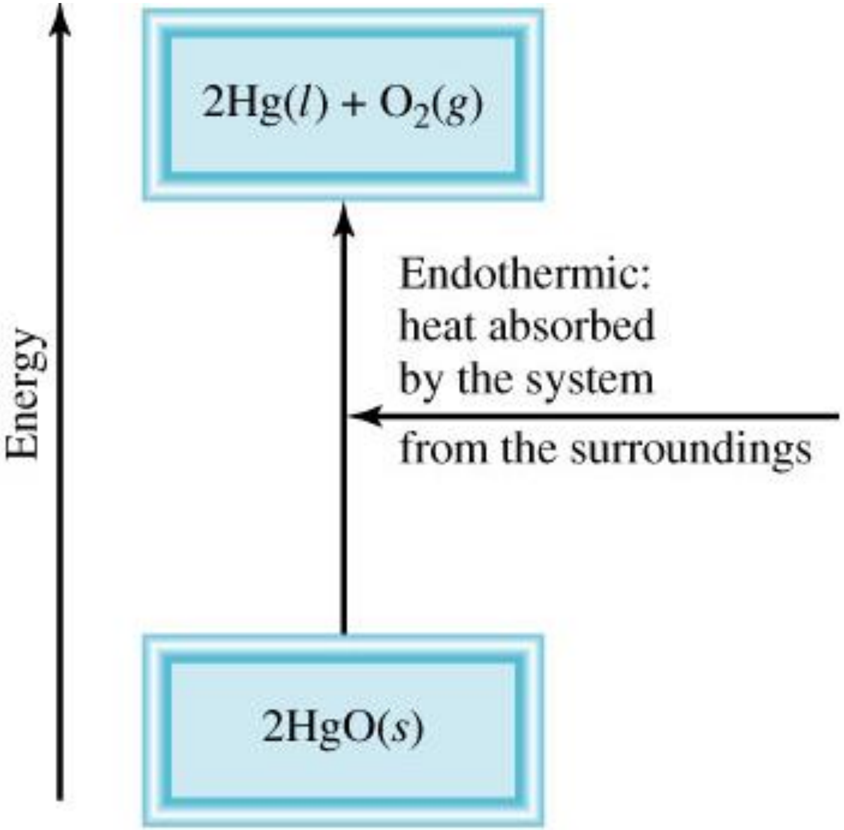
$2H_2(g) + O_2(g)$

Exothermic:
heat given off
by the system

to the surroundings

$2H_2O(l)$

Exothermic



Energy

$2Hg(l) + O_2(g)$

Endothermic:
heat absorbed
by the system

from the surroundings

$2HgO(s)$

Endothermic

$$\Delta H_{rxn} = \Sigma \Delta H_{products} - \Sigma \Delta H_{reactants}$$

$\Delta H_{rxn} < 0$ for exothermic reactions

$\Delta H_{rxn} > 0$ for endothermic reactions

Strongly exothermic reactions occur spontaneously.

Strongly endothermic reactions do not occur spontaneously.

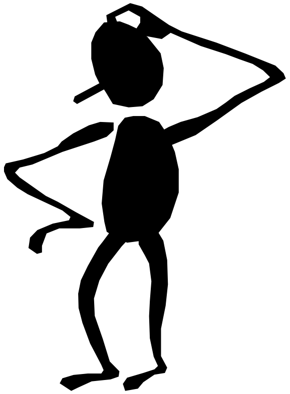
However;

Some weakly endothermic reactions occur spontaneously.

Some weakly exothermic reactions do not occur spontaneously.

This implies that enthalpy change alone cannot be used to judge the spontaneity of a chemical reaction.

<u>What else then ?</u>



Answer: A change in entropy

Entropy change (ΔS)

Change in entropy is the change in degree of randomness or disorder.

A definite amount of entropy is associated with each chemical species.

When a given chemical species is in the gaseous state, the molecules are disordered with respect to each other.

The entropy of this species in the gaseous state is much greater than when it is in the solid state, where the molecules are highly ordered with respect to each other.

So once again, entropy is the amount of disorder in a system.

The entropy of the universe increases in a spontaneous process.

Therefore, it would not be wrong to assume that the disorderliness of the universe is always increasing.

- ✓ A system will tend towards maximum entropy.
- ✓ The entropy drive of a chemical reaction will be towards the side with the most molecules in the most random phase:

gases $_{(g)}$ >> solutions $_{(aq)}$ > liquids $_{(l)}$ >> solids $_{(s)}$

- ✓ If both the enthalpy drive and the entropy drive favor the products, the reaction will be spontaneous
- ✓ If both the enthalpy drive and the entropy drive favor the reactants, the reaction will be non-spontaneous
- ✓ If the enthalpy and entropy drive are in opposite directions, the reaction will be reversible and is said to be in chemical equilibrium.

Summary

Favorable Conditions	Unfavorable Conditions
$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	$\Delta S < 0$

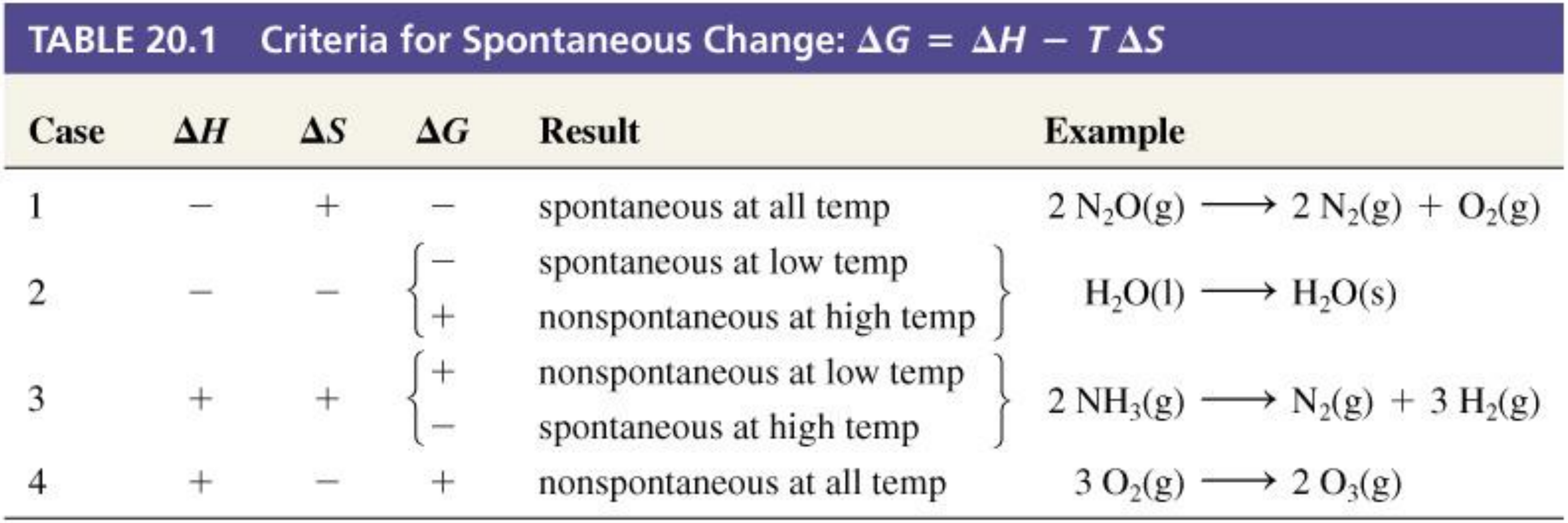


TABLE 20.1 Criteria for Spontaneous Change: $\Delta G = \Delta H - T\Delta S$

Case	ΔH	ΔS	ΔG	Result	Example
1	−	+	−	spontaneous at all temp	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
2	−	−	−	spontaneous at low temp	$H_2O(l) \longrightarrow H_2O(s)$
			+	nonspontaneous at high temp	
3	+	+	+	nonspontaneous at low temp	$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g)$
			−	spontaneous at high temp	
4	+	−	+	nonspontaneous at all temp	$3\,O_2(g) \longrightarrow 2\,O_3(g)$

What Makes a Reaction Spontaneous ?

So, based on the above discussion we can conclude that the actual driving force for a chemical reaction is a **combination of enthalpy change and entropy change**.

This driving force is called the GIBBS FREE ENERGY CHANGE, (ΔG) of the reaction.

Gibbs Free Energy (ΔG)

$$\left[\text{change in free energy}\right]=\left[\text{change in enthalpy}\right]-\left[\text{temperature}\right]\times\left[\text{change in entropy}\right]$$

$$\left(\mathbf{\Delta G}\right)=\ \mathbf{\Delta H-T\Delta S}$$

Experimental observations have shown that a decrease in free energy is associated with reactions which occur spontaneously.

When $\Delta G<0$ spontaneous, tendency to occur

When $\Delta G>0$ reaction will occur only if energy is supplied.

When $\Delta G=0$ reaction is at equilibrium.

$$\Delta G_{\text{rxn}} = \sum n\Delta G_{\text{products}} - \sum m\Delta G_{\text{reactants}}$$

Chemical thermodynamics

- tells us whether a particular reaction can be performed at all, and if it is possible,
- is necessary to help us find the best conditions for carrying out the reaction.

Free Energy of Formation

To provide a uniform basis for the calculation of the free energy change associated with a particular chemical reaction, standard state conditions for chemical systems are assigned.

- 1 atm pressure & 298 ^oK (25 ^oC)

- The concentrations of all aqueous solutions are 1 M.

A free energy change under standard state conditions is denoted by ΔG^0.

Free Energy of Formation

It is impossible to measure absolute values of free energy. We can only measure changes in free energy. To establish a baseline, a convention is necessary. Therefore,

- Every element is assigned a free energy of formation of zero at standard state.
- H^+ at a concentration of 1 mol/L in an ideal solution has a free energy of formation of zero at standard state.

Free Energy of Formation

The free energy change for chemical reaction is defined as the difference between free energies of the final and the initial states:

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

Under standard conditions

$$\Delta G^0_{\text{rxn}} = \sum n\Delta G^0_{\text{f, prod.}} - \sum m\Delta G^0_{\text{f, react.}}$$

Free Energy of Formation

$$\Delta G^0{}_{\text{rxn}} = \sum n\Delta G^0{}_{\text{f , prod.}} - \sum m\Delta G^0{}_{\text{f , react.}}$$

Note

$\Delta G^0{}_{\text{rxn}}$ is expressed in terms of kCal.

$\Delta G^0{}_{\text{f}}$ is expressed in terms of kCal/mol.

Therefore, $\Delta G^0{}_{\text{f}}$ values are multiplied by the molar coefficients in the balanced chemical equation to get $\Delta G^0{}_{\text{rxn.}}$

$C(\text{graphite}) + O_2\,(g) \longrightarrow CO_2\,(g)$ $\Delta G^0_{rxn} = \Delta G^0_{f,\,CO_2}$

$S(\text{rhombic}) + O_2\,(g) \longrightarrow SO_2\,(g)$ $\Delta G^0_{rxn} = \Delta G^0_{f,\,SO_2}$

Ex.

Fe^{2+} is present in groundwater under anaerobic conditions. When exposed to air, Fe^{2+} may slowly oxidize to Fe^{3+}, which forms an insoluble hydroxide precipitate. Is the following reaction spontaneous?

$$2\ Fe^{2+}_{(aq)} + HOCl_{(aq)} + 5\ H_2O_{(l)} \leftrightarrow 2\ Fe(OH)_{3(s)} + 2\ Cl^-_{(aq)} + 5\ H^+_{(aq)}$$

$$\Delta G^0_{\text{rxn}} = \sum m \Delta G^0_{\text{f , prod.}} - \sum n \Delta G^0_{\text{f , react.}}$$

$2\ Fe^{2+}{}_{(aq)} + HOCl_{\ (aq)} + 5\ H_2O_{(l)} \leftrightarrow 2\ Fe(OH)_{3(s)} + 2\ Cl^{-}{}_{(aq)} + 5\ H^{+}{}_{(aq)}$

	$\underline{\Delta G^0{}_{form}\ (kCal/mol)}$
Fe^{2+}	-20.30
$HOCl_{\ (aq)}$	-19.1
$H_2O_{(l)}$	-56.69
$Fe(OH)_{3(s)}$	-166.0
$Cl^{-}{}_{(aq)}$	-31.35

$$\Delta G^0{}_{rxn} = \left(2\times\text{-}166 + 2\times -31.35\ +\ 0\right)\ -\left(2\times\text{-}20.30 + (-19.1) + 5\times\text{-}56.69\right)$$

$\Delta G^0{}_{rxn} =\ -10.55$ kCal

$\Delta G^0{}_{rxn} < 0$, so the reaction is spontaneous.

- Our interest in an equilibrium system is often at <u>non-standard conditions</u>.
- So knowing Δ G° is usually not very useful.
- It applies to the situation at which all reactants and products are at standard state, i.e. 1 M concentration or gases at 1 atm pressure.

$$\Delta G^0_{\text{rxn}} = \sum m\Delta G^0_{\text{f , prod.}} - \sum n\Delta G^0_{\text{f , react.}}$$

Water and steam

$$H_2O\ (l,\ 1\ atm) \leftrightarrows H_2O\ (g,\ 1\ atm)$$

$$\Delta G^\circ_{373.15\ K} = 0\ kJ/mol$$

The system **is at equilibrium** at **1 atm (standard conditions)** and at the **boiling point temperature**!

www.chem.mun.ca/homes/pmhome/peter/19SpontaneousChange.ppt

Water and steam

$H_2O\ (l,\ 1\ atm) \leftrightarrows H_2O\ (g,\ 1\ atm)$

$\Delta G^\circ_{298.15\ K} = 8.590\ kJ/mol$

The system **is not at equilibrium** at **1 atm (standard conditions)** and at the **room temperature**!

www.chem.mun.ca/homes/pmhome/peter/19SpontaneousChange.ppt

Water and steam

$H_2O\ (l,\ 1\ atm) \leftrightarrows H_2O\ (g,\ 1\ atm)$

$$\Delta G^\circ_{298.15\ K} = 8.590\ kJ/mol$$

The **forward process is <u>non-spontaneous</u>** (**$\Delta G^\circ > 0$**) so the **reverse process is <u>spontaneous</u>** and condensation occurs.

www.chem.mun.ca/homes/pmhome/peter/19SpontaneousChange.ppt

Water and steam

$$H_2O\ (l,\ 0.03126\ atm) \leftrightarrows H_2O\ (g,\ 0.03126\ atm)$$

$$\Delta G_{298.15\ K} = 0\ kJ$$

The system **is at equilibrium** at **0.03126 atm (non-standard conditions)** and at the **room temperature**!

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Water and steam

H_2O (l, 0.03126 atm) $\leftrightarrows$

H_2O (g, 0.03126 atm)

$\Delta G_{298.15\ K} = 0\ kJ/mol$

Water **CAN** evaporate at **room temperature,**

just <u>not</u> to give an equilibrium pressure of 1 atm!

www.chem.mun.ca/homes/pmhome/peter/19SpontaneousChange.ppt

$$G_i = \Delta G^0_{f,i} + RT \ln[i] \rightarrow \text{nonstandard state}$$

Now, let us use this information to determine the free energy change of the reaction in which calcite dissolves in acid to form calcium and bicarbonate ions at non-standard state.

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$

Substance	ΔG^0_f (kCal/mol)
$CaCO_3$	-269.78 kCal/mol
Ca^{2+}	-132.18 kCal/mol
HCO_3^-	-40.31 kCal/mol

$$\Delta G_{rxn} = [\ \Delta G_{f,HCO_3^-} + \Delta G_{f,Ca^{2+}}\ ] - [\ \Delta G_{f,CaCO_3} + \Delta G_{f,H^+}\ ]$$

$$\Delta G_{rxn} = \left(\Delta G^0{}_{f,HCO_3^-} + RT \ln[HCO_3{}^-] + \Delta G^0{}_{f,Ca^{2+}} + RT \ln[Ca^{2+}] \right)$$

$$- \left(\Delta G^0{}_{f,CaCO_3} + RT \ln[CaCO_3] + \Delta G^0{}_{f,H^+} + RT \ln[H^+] \right)$$

$$\Delta G_{rxn} = \left(\Delta G^0{}_{f,HCO_3^-} + \Delta G^0{}_{f,Ca^{2+}} \right) - \left(\Delta G^0{}_{f,CaCO_3} + \Delta G^0{}_{f,H^+} \right)$$

$$+ RT \ln[HCO_3{}^-] + RT \ln[Ca^{2+}] - RT \ln[CaCO_3] - RT \ln[H^+]$$

$$\Delta G_{rxn} = \Delta G^{0}_{rxn} + RT \ln\left(\frac{[HCO_3^-][Ca^{2+}]}{[CaCO_3][H^+]}\right)$$

$$\Delta G_{rxn} = \Delta G^{0}_{rxn} + RT \ln Q$$

where Q is the ***reaction quotient.***

When the chemical system is at equilibrium,

$\Delta G_{rxn} = 0$ and $Q = K_{eq}$

$$0 = \Delta G^0{}_{rxn} + RT \ln K_{eq}$$

$$\Delta G^0{}_{rxn} = - RT \ln K_{eq}$$

*Note that this equation applies to 25^{o}C since $\Delta G^0{}_{rxn}$ is given for 25^{o}C.

- This equation shows the relationship between the standard free energy change and the **thermodynamic equilibrium constant.**
- It is one of the most important in chemistry because it relates the equilibrium composition of a chemical reaction system to measurable physical properties of the reactants and products.

- If you know the entropies and the enthalpies of formation of a set of substances, you can predict the equilibrium constant of any reaction involving these substances without the need to know anything about the mechanism of the reaction.

Table 3.1 Standard Free Energies and Enthalpies of Formation at 25˚C

Reference : Sawyer, McCarty, Parkin, *Chemistry for Environmental Engineering and Science*,
5th Edition, McGraw-Hill, 2003. page 56

Substance	State*	ΔG_f° , kJ/mol	ΔH_f° , kJ/mol
Ca^{2+}	aq	-553.6	-542.8
$CaCO_3$	s	-1128.76	-1206.87
CaF_2	s	-1175.6	-1228.0
$Ca(OH)_2$	s	-896.76	-986.6
$CaSO_4$	s	-1322.0	-1434.5
CH_4	g	-50.79	-74.6
CH_3CH_3	g	-32.89	-84.67
CH_3COOH	aq	-399.6	-488.4
CH_3COO^-	aq	-369.41	-486.0
CH_3CH_2OH	l	-174.8	-277.7
$C_6H_{12}O_6$	aq	-917.22	

*aq=aqueous, s=solid, l=liquid   Note: 1 kCal = 4.184 kJ

Substance	State*	ΔG_f° , kJ/mol	ΔH_f° , kJ/mol
Cl_2	g	0	0
Cl_2	aq	6.9	-23.4
Cl^-	aq	-131.3	-167.20
CO_2	g	-394.38	-393.51
CO_3^{2-}	aq	-527.80	-677.10
F^-	aq	-278.8	-332.6
Fe^{2+}	aq	-78.87	-89
Fe^{3+}	aq	-4.6	-48.5
HCO_3^-	aq	-586.85	-692.00
H_2CO_3	aq	-623	-699

*aq=aqueous, s=solid, l=liquid   Note: 1 kCal = 4.184 kJ

Substance	State*	ΔG_f° , kJ/mol	ΔH_f° , kJ/mol
H_2O	l	-237.18	-285.80
H_2O	g	-228.60	-241.8
HS^-	aq	12.05	-17.6
H_2S	g	-33.4	-20.6
H_2S	aq	-27.87	-39.3
H_2SO_4	l	-690.0	-814
Mg^{2+}	aq	-454.8	-466.9
$Mg(OH)_2$	s	-833.5	-924.5
Na^+	aq	-261.9	-240.1
*aq=aqueous, s=solid, l=liquid Note: 1 kCal = 4.184 kJ			

Substance	State*	ΔG_f° , kJ/mol	ΔH_f° , kJ/mol
NH_3	g	-16.4	-45.9
NH_3	aq	-26.65	-80.83
NH_4^+	aq	-79.37	-132.5
NO_2^-	aq	-37.2	-104.6
NO_3^-	aq	-111.34	-207.4
O_2	g	0	0
O_2	aq	16.32	-11.71
OH^-	aq	-157.2	-230.0
S^{2-}	aq	79.5	30.1
SO_4^-	aq	-744.63	-909.3
Zn^{2+}	aq	-147.1	-153.9
ZnS	s	-201.3	-206.0

*aq=aqueous, s=solid, l=liquid   Note: 1 kCal = 4.184 kJ

Ex. Using the given data, calculate the equilibrium constant for the reaction

$$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$$

	$H^+_{(aq)}$	$OH^-_{(aq)}$	$H_2O_{(l)}$
ΔH^0_f, kJ/mol	0	–230.0	–285.8
S^0, J/K·mol	0	–10.8	70.0

Solution: From the above data, we can evaluate the following quantities:

$$\Delta H^0{}_{\mathrm{rxn}} = \left(\sum \mathrm{m}\Delta H^0{}_{\mathrm{f\ products}}\right) - \left(\sum \mathrm{n}\Delta H^0{}_{\mathrm{f\ reactants}}\right) = (-230) - (-285.8) = +55.8\ \mathrm{kJ}$$

$$\Delta S^0{}_{\mathrm{rxn}} = \left(\sum \mathrm{m}\Delta S^0{}_{\mathrm{f\ products}}\right) - \left(\sum \mathrm{n}\Delta S^0{}_{\mathrm{f\ reactants}}\right) = (-10.8) - (70.0) = -\ 80.8\,\mathrm{J}/K$$

The value of ΔG^0 at 298K is

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

$$=(55800) - (298)(-80.8) = 79900\ \mathrm{J/mol}$$

$$K_{eq} = \exp\left(79900/(8.314 \times 298)\right) = e^{-32.2} = 1.01 \times 10^{-14}$$

Ex. The tap water in a town has the following characteristics.

$[HCO_3^-] = 10^{-3}$ M $[Ca^{2+}] = 10^{-3}$ M pH = 8.0

Will this water dissolve or precipitate $CaCO_3$? Which way the reaction will proceed at 25^0C ?

$$CaCO_{3(s)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$

Substance	**ΔG^0_f (kCal/mol)**
$CaCO_3$	-269.78 kCal/mol
Ca^{2+}	-132.18 kCal/mol
HCO_3^-	-140.31 kCal/mol

R= 1.98×10⁻³ kCal/mol.K

$$\Delta G^0_{rxn} = \left[\left(-132.18\right) + \left(-140.31\right)\right] - \left[\left(-269.78\right)\right] = -2.71 \text{ kCal}$$

$$-2.71 \text{ kCal} = (-1.98\times10^{-3} \text{ kCal/mol.K}) \times (298 \text{ K}) \times (\ln K_{eq})$$

$\ln K_{eq} = 4.59$ → **K_{eq}= 98.5** at 298 K or 25 ^oC

$$Q = \frac{[HCO_3^-][Ca^{2+}]}{[CaCO_{3(s)}][H^+]}$$

Compare Q with K_{eq}

At pH = 8.0 ⇨ Q= 100

$Q > K_{eq}$ only slightly 100 > 98.5

slightly precipitation

At pH = 7.0 ⇨ Q= 10

$Q < K_{eq}$

10 < 98.5 no precipitation

Temperature Dependence of Equilibrium Constant

- In most cases the reactions of interest in process chemistry are conducted at temperatures other than 25^{o}C. Therefore, it may be necessary to adjust equilibrium constants for nonstandard state temperatures.
- The standard-state free energy of reaction is a measure of how far the standard-state is from equilibrium.

$$\Delta G^0 = - RT \ln K_{eq}$$

But the magnitude of depends on the temperature of the reaction.

$$\mathbf{\Delta G^0 = \Delta H^0 - T\Delta S^0}$$

As a result, the equilibrium constant must depend on the temperature of the reaction.

Combining Eq’n.s 1 and 2 we obtain

$$-\mathrm{RT}\ \ln \mathrm{K}_{\mathrm{eq}} = \mathbf{\Delta H}^{0} - \mathbf{T\Delta S}^{0}$$

and

$$\ln \mathrm{K} = -\frac{\mathbf{\Delta H}^{0}}{\mathrm{RT}} + \frac{\mathbf{\Delta S}^{0}}{\mathrm{R}}$$

Remember that the enthalpy and entropy changes are regarded as constants with respect to temperature, so the equilibrium constant is exponentially dependent on temperature.

We often want to know how a change in temperature will affect the value of an equilibrium constant whose value is known at some fixed temperature. Suppose that the equilibrium constant has the value K_1 at temperature T_1 and we wish to estimate K_2 at temperature T_2.

$$\ln K_1 = \frac{-\Delta H^0}{RT_1} - \frac{\Delta S^0}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^0}{RT_2} - \frac{\Delta S^0}{R}$$

Subtracting ln K_2 from ln K_1 we obtain

$$\ln K_1 - \ln K_2 = -\left(\frac{\Delta H^0}{RT_1} - \frac{\Delta H^0}{RT_2} \right)$$

which is most conveniently expressed as

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

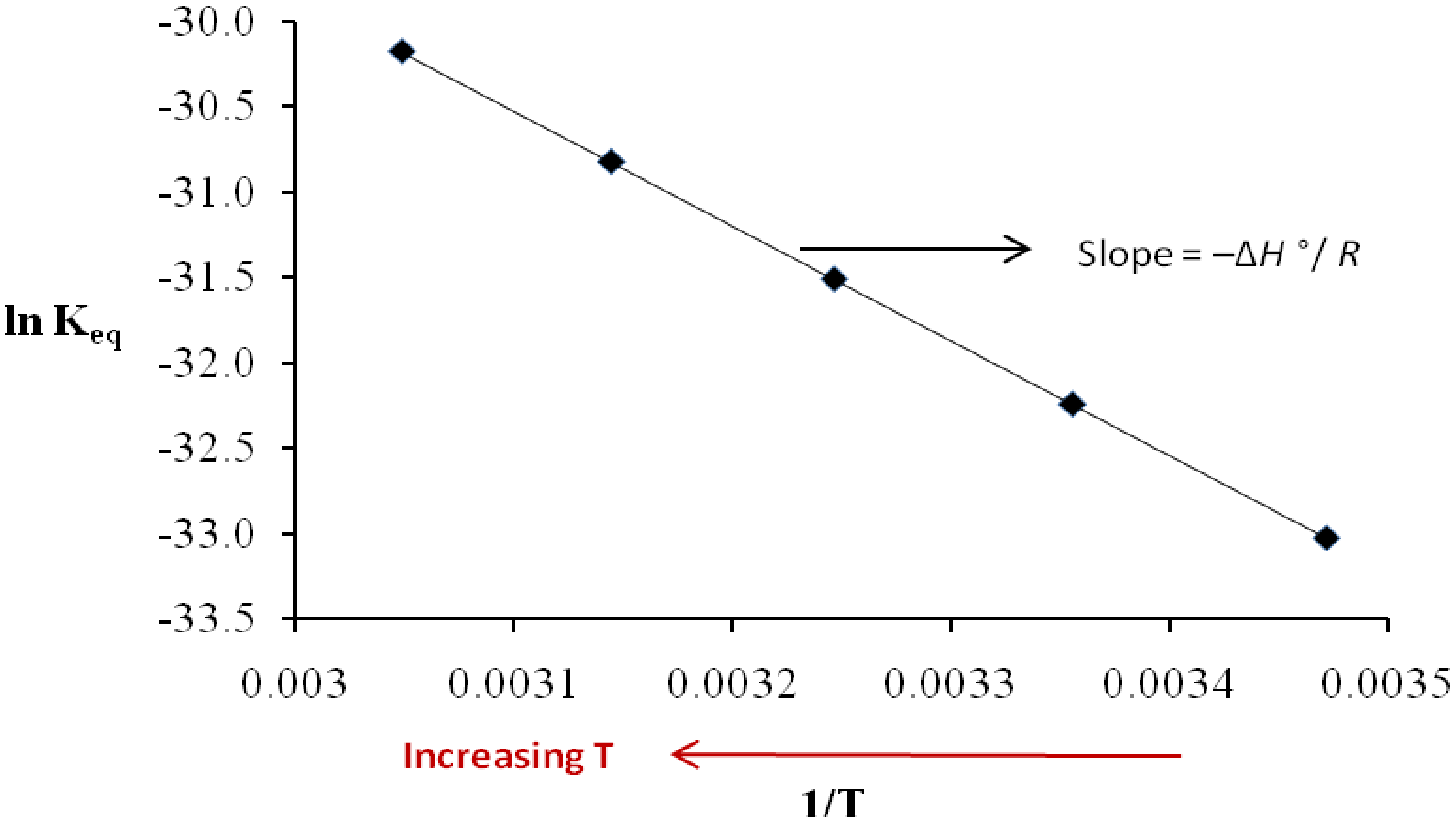
Above equation is called the ***van't Hoff equation.***

Ex. Plot the ln K_{eq} versus 1/T graph of

$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$

$\Delta H^0_{rxn} = +55.8$ kJ/mol

t (^{o}C)	**T (^{o}K)**	**1/T**	**ln** K_{eq} **=**	K_{eq} **=**
15	288	0,003472	-33,0	4,6E-15
25	298	0,003356	-32,2	1,0E-14
35	308	0,003247	-31,5	2,1E-14
45	318	0,003145	-30,8	4,1E-14
55	328	0,003049	-30,2	7,8E-14

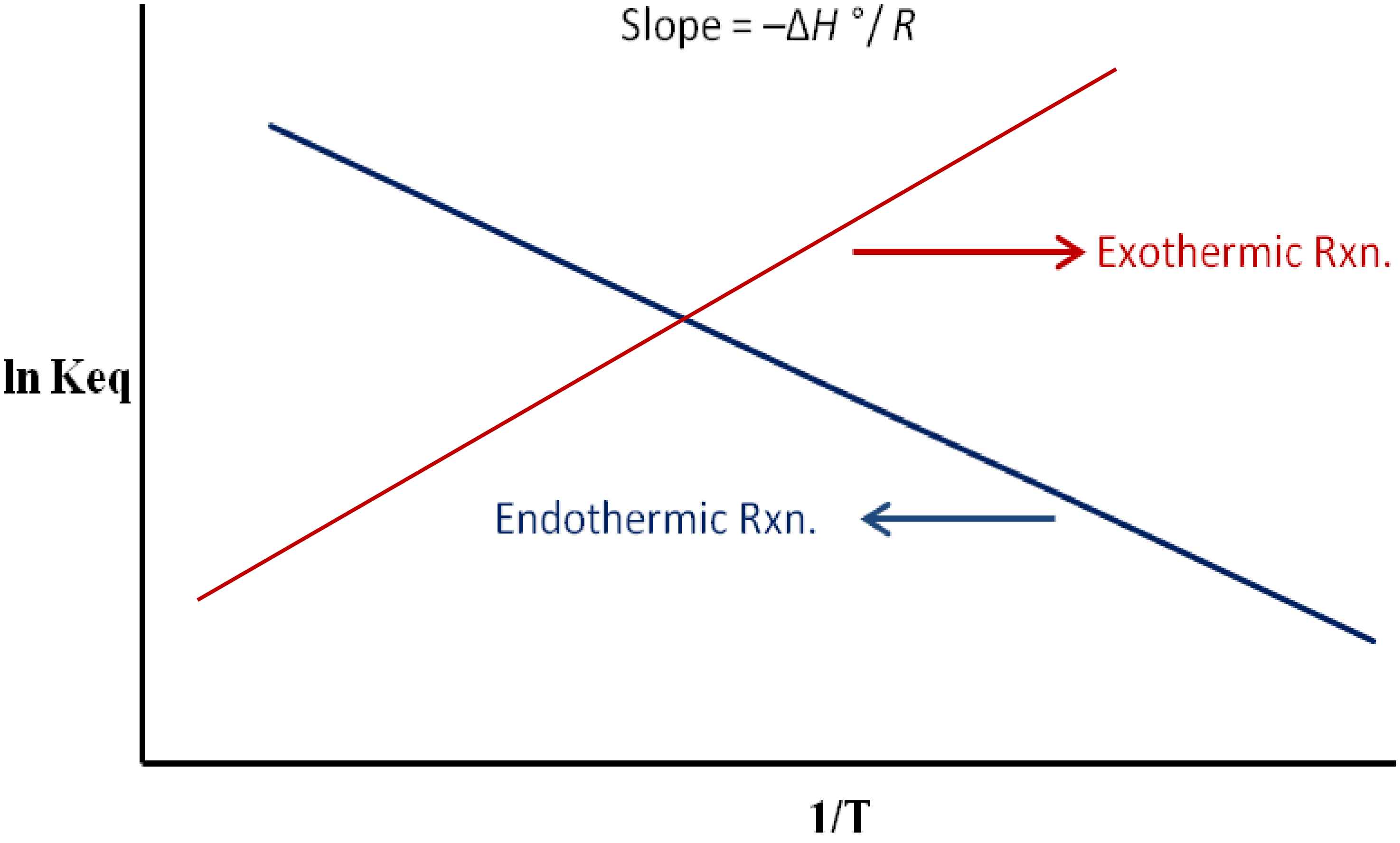


Slope = $-\Delta H°/R$

Increasing T

Note that the reaction is endothermic (ΔH^0_{rxn} = +55.8 kJ/mol), and K_{eq} increases with temperature. For exothermic reactions however, K_{eq} decreases with temperature.

Change	**Exothermic Reaction**	**Endothermic Reaction**
Increase temperature	K_{eq} decreases	K_{eq} increases
Decrease temperature	K_{eq} increases	K_{eq} decreases


Slope = −ΔH °/ R
Exothermic Rxn.
ln Keq
Endothermic Rxn.
1/T

Ex. A municipal water supply enters a residence at 15°C and is heated to 60°C in the home water heater. If the water is just saturated with respect to $CaCO_{3(s)}$ at 25°C, what will be the condition of water (i.e. oversaturated or undersaturated) with respect to $CaCO_{3(s)}$

i. as it enters the residence and
ii. as it leaves the water heater?

$$CaCO_{3(s)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$

Substance	**ΔH^0_f (kCal/mol)**
$CaCO_{3(s)}$	-288.45 kCal/mol
Ca^{2+}	-129.77 kCal/mol
HCO_3^-	-165.18 kCal/mol

Using Eq’n 2, we have already calculated that K_{eq} is 98.8 at 25°C. Now, using the van’t Hoff equation we can calculate the values of K_{eq} at 15°C and 60°C. Then, we can compare K_{15} and K_{60} with the reaction quotient Q and decide whether the water is undersaturated or oversaturated.

If Q $> K_{eq}$ water is oversaturated.
If Q $< K_{eq}$ water is undersaturated.

$$\ln\frac{K_1}{K_2} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta H^0{}_{rxn} = \left(\sum \Delta H^0{}_{f,\ \text{products}}\right) - \left(\sum \Delta H^0{}_{f,\ \text{reactants}}\right)$$

$$\Delta H^0{}_{rxn} = (-129.77) + (-165.18) - (-288.45) = -6.5\ \text{KCal}/\text{mol}$$

$$\ln\left(\frac{K_{15}}{K_{25}}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{288} - \frac{1}{298}\right)$$

$$\ln\left(\frac{K_{15}}{98.8}\right) = -\frac{-6.5}{1.98\times10^{-3}}\left(\frac{1}{288} - \frac{1}{298}\right)$$

$K_{15} = 141.3$

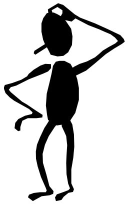
$$\ln\left(\frac{K_{60}}{K_{25}}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{333} - \frac{1}{298}\right)$$

$$\ln\left(\frac{K_{60}}{98.8}\right) = -\frac{6.5}{1.98\times10^{-3}}\left(\frac{1}{333} - \frac{1}{298}\right)$$

$K_{60} = 30.2$

	15 ºC	**25 ºC**	**60 ºC**
K_{eq}	141.3	98.8	30.2

What is the value of Q?



$$Q = \frac{[HCO_3^-][Ca^{2+}]}{[H^+]}$$

Note that water is saturated with respect to $CaCO_{3(s)}$ at 25 ^{o}C. Therefore, Q is 98.8.

$$98.8 = \frac{[HCO_3^-][Ca^{2+}]}{[H^+]}$$

At 15^{o}C	$Q < K_{eq}$	(98.8 < 141.3)	water is undersaturated.
At 60^{o}C	$Q > K_{eq}$	(98.8 >30.2)	water is oversaturated.