Reaction Gibbs Energy

The reaction Gibbs energy, $\Delta_r G$, is the slope of the Gibbs energy as a function of the extent of reaction, ξ , in moles.

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

Expressed in terms of chemical potentials, if the reaction $A \rightarrow B$ progresses by d ξ , then

$$\mathrm{d}G = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} = -\mu_{\mathrm{A}}\,\mathrm{d}\xi + \mu_{\mathrm{B}}\mathrm{d}\xi = (\mu_{\mathrm{B}} - \mu_{\mathrm{A}})\mathrm{d}\xi$$

Thus,

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

Because chemical potentials vary with the composition of a reacting mixture, the slope of the G vs. ξ plot changes as the reaction proceeds. It is negative when $\mu_A > \mu_B$ and positive when $\mu_A < \mu_B$. The slope becomes zero at equilibrium, *i.e.*, when $\mu_A = \mu_B$, at which point $\Delta_r G = 0$.

 $\Delta_{\rm r}G < 0$ when the forward reaction is spontaneous (exergonic, *i.e.*, work-producing). $\Delta_{\rm r}G > 0$ when the reverse reaction is spontaneous (endergonic, *i.e.*, work-consuming).

Reaction Gibbs Energy



Extent of reaction, ξ

Figure 6A.1 As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope at the foot of the valley.

Coupled Reactions



Figure 6A.2 If two weights are coupled as shown here, then the heavier weight will move the lighter weight in its nonspontaneous direction: overall, the process is still spontaneous. The weights are the analogues of two chemical reactions: a reaction with a large negative ΔG can force another reaction with a smaller ΔG to run in its non-spontaneous direction.

$$\begin{array}{ll} {\rm glucose} \ + {\rm fructose} \leftrightarrows {\rm sucrose} & \Delta G = +27 \ {\rm kJ}/\\ {\rm ATP} + {\rm H}_2 {\rm O} \leftrightarrows {\rm ADP} + {\rm P}_i & \Delta G = -30 \ {\rm kJ}/ \end{array}$$

glucose + fructose + ATP \rightleftharpoons sucrose + ADP + P_i $\Delta G = -3kJ/$

Uncoupled reaction:

$$ightarrow for the formula of the formula of$$

Coupled Reactions



Perfect Gas Equilibria

For the equilibrium reaction $A \rightleftharpoons B$ if A and B are perfect gases, then since $\Delta_r G^\circ = \mu_B^\circ - \mu_A^\circ$ $\Delta_r G = \mu_B^\circ - \mu_A^\circ = (\mu_B^\circ + RT \ln (p_B / p^\circ) - (\mu_A^\circ + RT \ln (p_A / p^\circ)))$

$$\Delta_r G = \mu_B \quad \mu_A = (\mu_B + RT \ln (p_B / p)) \quad (\mu_A + RT \ln (p_A / p))$$
$$\Delta_r G = \Delta_r G^\circ + RT \ln (p_B / p_A)$$

Letting the ratio of partial pressures, p_B/p_A , be denoted by Q, the reaction quotient, then

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

The standard reaction Gibbs energy, $\Delta_r G$, is the difference between the standard molar Gibbs energies of the reactants and products. Thus,

$$\Delta_r G^\circ = G_m^\circ(B) - G_m^\circ(A) = \mu_B^\circ - \mu_A^\circ$$
$$= G_f^\circ(B) - G_f^\circ(A)$$

where $\Delta_f G^o$ is the standard Gibbs energy of formation.

Perfect Gas Equilibria

At equilibrium, $\Delta_r G = 0$. Thus, letting the ratio of the two partial pressures at equilibrium be represented by *K*, the equilibrium constant,

or $0 = \Delta_r G^o + RT \ln K$ $\Delta_r G^o = -RT \ln K$ (Eq. 6A.8) Thus, $K = \exp\left(-\frac{\Delta_r G^o}{RT}\right) = \left(\frac{p_B}{p_A}\right)_{\text{equil.}}$

Eq. 6A.8 is one of the most important equations in chemical thermodynamics because it serves as the crucial link between thermodynamic data, such as enthalpies of formation, molar entropies, and Gibbs energies of formation, and the equilibrium composition of a chemical reaction.

When $\Delta_r G^o > 0$, then K < 1 and $pA > p_B$, *i.e.*, reactant A is predominant at equilibrium.

When $\Delta_r G^{\theta} < 0$, then K > 1 and $p_B > p_A$, *i.e.*, product B is predominant at equilibrium.

Perfect Gas Equilibria

The minimum in Gibbs energy that exists at equilibrium, as depicted in Fig. 6A.1, is a result of the Gibbs energy of mixing of gases A and B:

$$\Delta_{mix}G = nRT \left(x_A \ln x_A + x_B \ln x_B \right) \qquad (Eq. \ 5A.16)$$

If $\Delta_{mix}G$ were not included, the Gibbs energy would decline linearly with increasing extent of reaction, ξ , with no minimum (upper line).

However, because of the entropy effect as A decreases and B increases, the resulting mixing of A and B causes an additional decrease in G (lower curve) that results in a minimum in G at a certain value of ξ (middle curve), which corresponds to the equilibrium position of the reaction.



Figure 6A.3 If the mixing of reactants and products is ignored, then the Gibbs energy changes linearly from its initial value (pure reactants) to its final value (pure products) and the slope of the line is $\Delta_r G^{\ominus}$. However, as products are produced, there is a further contribution to the Gibbs energy arising from their mixing (lowest curve). The sum of the two contributions has a minimum. That minimum corresponds to the equilibrium composition of the system.

Chemical reactions can be represented symbolically using the following notation:

$$\sum_{J} v_{J} J = 0$$

where J denotes each individual reactant and product, and v_J are the corresponding stoichiometric coefficients in the chemical reaction, with v_J for reactants being negative and those for products being positive.

For the reaction $2A + B \rightarrow 3C + 2D$, for example, the values of v_J are $v_A = -2$, $v_B = -1$, $v_C = +3$, and $v_D = +2$. The extent of reaction, ξ , is then defined so that for any $\Delta\xi$ the corresponding change in the amount of any reaction component *J* is given by $v_J\Delta\xi$.

For the above reaction, for example,

$$Q = a_C^3 \times a_D^2 \times a_A^{-2} \times a_B^{-1} = \frac{a_C^3 \times a_D^2}{a_A^2 \times a_B}$$

Because $\Delta_r G = \Delta_r G^{\circ} + RT \ln Q$, then

$$\Delta_r G = \sum_{\text{Products}} \nu \Delta_f G^{\circ} + \sum_{\text{Reactants}} \nu \Delta_f G^{\circ} = \sum_{\text{J}} \nu_J \Delta_f G^{\circ}(\text{J})$$

where the v_J are the (signed) stoichiometric coefficients.

The reaction quotient, Q, always has the following form:

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} = \prod_{J} a_{J}^{v_{J}}$$

where the activity, a_J , of each component *J* is given by $a_J = \gamma_J x_J$. Here, γ_J is the so-called *activity coefficient*, which essentially corrects for non-ideal behavior of solutes in solution, and x_J is a concentration unit, such as mole fraction, molality, or molarity. It is analogous to the fugacity coefficient, φ , that corrects for the non-ideal behavior of gases, $f = \varphi p$. Activity coefficients vary with the identity of the solute and approach unity with decreasing concentration:

$$a_J \rightarrow x_J$$
 and $\gamma_J \rightarrow 1$ as $x_J \rightarrow 0$

Similarly,

$$\varphi \to 1$$
 as $p \to 0$

At equilibrium, $\Delta_r G = 0$ and Q = K, so that

$$K = Q_{\text{equil}} = \left(\prod_{J} a_{J}^{\nu_{J}}\right)_{\text{equil}}$$

When *K* is expressed in terms of activities (or fugacities, in the case of gases), it is termed a **thermodynamic equilibrium constant**.

Activities are dimensionless numbers, so K also must be dimensionless. For approximate calculations involving K, activities are often replaced with the following terms, particularly in dilute solutions or at low gas pressures:

State	Measure	Approximation for <i>a</i> _J	Definition
Solute	molality	$b_{\mathrm{J}}/b_{\mathrm{J}}^{\ominus}$	$b^{\ominus} = 1 \mod \text{kg}^{-1}$
	molar concentration	[J]/c⇔	$c^{\ominus} = 1 \operatorname{mol} \mathrm{dm}^{-3}$
Gas phase	partial pressure	$p_{\rm J}/p^{\ominus}$	$p^{\ominus} = 1$ bar

Setting up Equilibrium Constants

Example One:

$$N_2(g) + 3H_2(g) \stackrel{\rightarrow}{\leftarrow} 2NH_3(g)$$

$$K_a = \frac{a_{NH_3}^2}{a_{H_2}^3 a_{N_2}} \approx \frac{P_{NH_3}^2 \left(P^\theta\right)^2}{P_{H_2}^3 P_{N_2}} = \frac{X_{NH_3}^2}{X_{H_2}^3 X_{N_2}} \left(\frac{P^\theta}{P}\right)^2$$

(K_a is unitless.)

 $K_P = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}}$ K_p use pressures instead of activity K_p has units, which vary depending on stoichiometry of reaction. Numerically, K_p = K_a for ideal gases if partial pressures are in bar.

What are the units of K_p for the following reaction, assuming that the pressures are given in bar?

 $2\mathrm{H}_{2}(g) + \mathrm{S}_{2}(g) \to 2\mathrm{H}_{2}\mathrm{S}(g)$

- A) bar
- B) bar $^{-1}$
- C) bar 2
- D) Unitless

Example Two:
$$Fe_2O_3(s) + CO(g) \xrightarrow{\longrightarrow} 2FeO(s) + CO_2(g)$$
 $K_a = \frac{a_{FeO}^2 a_{CO_2}}{a_{Fe_2O_3} a_{CO}} \approx \frac{P_{CO_2}}{P_{CO}} = \frac{X_{CO_2}}{X_{CO}}$

Equilibrium Constants at High Pressure

For ideal gases, to calculate K_a , just use $a = P/P^{\theta}$ At high pressure, can't assume ideal gas. For real gases, just use $a = f/f^{\theta} = \phi P/P^{\theta}$ For real gases, can relate K_a and K_p

$$K_{p} = \frac{K_{a} \left(P^{\theta}\right)^{\Delta v_{g}}}{K_{\phi}}$$

where Δv_g is the change in moles of gas for a reaction. K_{ϕ} is a constant made up of the fugacity coefficients for a reaction. Example: A mixture of CO(g), H₂(g) and CH₃OH(g) at 500 K with P_{CO}=10 bar, P_{H2}= 1 bar and P_{CH3OH}= 0.1 bar is passed over a catalyst. Can more methanol be formed? $\Delta_{rxn}G^{\theta} = 21.21$ kJmol⁻¹ $\Delta_{rxn}G = \Delta_{rxn}G^{\theta} + RT \ln Q$

What if initial pressures are $P_{CO}=1$ bar, $P_{H_2}=10$ bar and PCH₃OH=0.1 bar?

Although equilibrium constants in terms of activities are exact, it is often convenient to express them in concentration units to calculate approximate results. For the reaction $A + B \rightleftharpoons C + D$, for example,

$$K_a = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_{\gamma} K_b$$

where b refers to molality. For very dilute solutions, it can often be assumed that $K_{\gamma} \approx 1$, so that $K \approx K_{b}$. The same approximation can apply to molarities.

If the equilibrium constant for a gas-phase reaction needs to be expressed in terms of molar concentrations instead of partial pressures, and if the gases can be treated as perfect, then the p_J terms that appear in *K* can be replaced by [J]*RT*, so that

$$K = \prod_{J} a_{J}^{\nu_{J}} = \prod_{J} \left(\frac{p_{J}}{p^{\circ}} \right)^{\nu_{J}} = \prod_{J} [J]^{\nu_{J}} \left(\frac{RT}{p^{\circ}} \right) = \prod_{J} [J]^{\nu_{J}} \times \prod_{J} \left(\frac{RT}{p^{\circ}} \right)^{\nu_{J}}$$

where the concentration (molarity) of J is given by:

$$[J] = \frac{n}{V}$$

Relation between equilibrium constants

The (dimensionless) equilibrium constant K_c is then

$$K_{c} = \prod_{J} \left(\frac{[J]}{c^{\circ}}\right)^{v_{J}}$$
$$K = K_{c} \times \prod_{J} \left(\frac{c^{\circ}RT}{p^{\circ}}\right)^{v_{J}} = K_{c} \times \left(\frac{c^{\circ}RT}{p^{\circ}}\right)^{\Delta v}$$

Thus,

where $\Delta v = \Sigma_J v_J$, which is the change (+ or –) in stoichiometric number of gaseous moles in the reaction, *i.e.*, v (gas-phase products) – v (gas-phase reactants).

Reactions	TABLE 5G.2 Equilibrium Constants for Various Reactions				
for which $\Delta v = 0$	Reaction	<i>T</i> /K*	K	$K_{ m c}^{\ \dagger}$	
	$H_2(g) + Cl_2(g) \rightleftharpoons 2 HCl(g)$	300	$4.0 imes 10^{31}$	$4.0 imes 10^{31}$	
		500	$4.0 imes10^{18}$	$4.0 imes10^{18}$	
		1000	$5.1 imes10^8$	$5.1 imes10^8$	
	$H_2(g) + Br_2(g) \rightleftharpoons 2 HBr(g)$	300	$1.9 imes10^{17}$	$1.9 imes10^{17}$	
		500	$1.3 imes10^{10}$	$1.3 imes10^{10}$	
		1000	$3.8 imes10^4$	$3.8 imes10^4$	
	$H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$	298	794	794	
		500	160	160	
		700	54	54	
	$2 \operatorname{BrCl}(g) \Longrightarrow \operatorname{Br}_2(g) + \operatorname{Cl}_2(g)$	300	377	377	
		500	32	32	
		1000	5	5	
	$2 \text{ HD}(g) \rightleftharpoons H_2(g) + D_2(g)$	100	0.52	0.52	
	40000000 (4000000) (40000000)	500	0.28	0.28	
		1000	0.26	0.26	

Reactions for which $\Delta v \neq 0$	$F_2(g) \Longrightarrow 2 F(g)$	500 1000 1200	3.0×10^{-11} 1.0×10^{-2} 0.27	7.3×10^{-13} 1.2×10^{-4} 2.7×10^{-3}
	$\operatorname{Cl}_2(g) \rightleftharpoons 2 \operatorname{Cl}(g)$	1000 1200	$1.0 imes 10^{-5} \ 1.7 imes 10^{-3}$	$1.2 imes 10^{-7}$ $1.7 imes 10^{-5}$
	$Br_2(g) \rightleftharpoons 2 Br(g)$	1000 1200	$3.4 imes 10^{-5}$ $1.7 imes 10^{-3}$	$4.1 imes 10^{-7}$ $1.7 imes 10^{-5}$
	$I_2(g) \rightleftharpoons 2 I(g)$	800 1000 1200	2.1×10^{-3} 0.26 6.8	3.1×10^{-5} 3.1×10^{-3} 6.8×10^{-2}
	$N_2(g) + 3 H_2(g) \Longrightarrow 2 NH_3(g)$	298 400 500	$6.8 imes 10^{5}$ 41 $3.6 imes 10^{-2}$	$4.2 imes 10^{8} \\ 4.5 imes 10^{4} \\ 62$
	$2 \operatorname{SO}_2(g) + \operatorname{O}_2(g) \rightleftharpoons 2 \operatorname{SO}_3(g)$	298 500 700	$4.0 imes 10^{24} \ 2.5 imes 10^{10} \ 3.0 imes 10^4$	$9.9 imes 10^{25} \ 1.0 imes 10^{12} \ 1.7 imes 10^{6}$
	$N_2O_4(g) \rightleftharpoons 2 NO_2(g)$	298 400 500	0.15 47.9 $1.7 imes 10^3$	$6.1 imes 10^{23}$ 1.44 41

Molecular Interpretation of Equilibrium Constant

$$\Delta_{r}G = -RTlnK$$
$$\Delta_{r}H - T\Delta_{r}S = -RTlnK$$
$$-\frac{\Delta_{r}H}{RT} + \frac{\Delta_{r}S}{R} = lnK$$
$$K = e^{-\frac{\Delta_{r}H}{RT} + \frac{\Delta_{r}S}{R}}$$

More closely-spaced energy levels means higher entropy. Thus, favorable entropy effects may dominate over adverse energy effects, as in the endothermic reaction whose energy levels are depicted in Fig. 6A.4.



Figure 6A.4 The Boltzmann distribution of populations over the energy levels of two species A and B with similar densities of energy levels. The reaction $A \rightarrow B$ is endothermic in this example. (a) The bulk of the population is associated with the species A, so that species is dominant at equilibrium. (b) Even though the reaction $A \rightarrow B$ is endothermic, the density of energy levels in B is so much greater than that in A that the population associated with B is greater than that associated with A, so B is dominant at equilibrium.

Response of Equilibrium to the Conditions

LeChatelier's Principle: When subjected to a disturbance, a system at equilibrium responds in a way that tends to minimize the effect of the disturbance.

• Effect of Pressure

If moles gaseous products = moles gaseous reactants, changing total P of reactants does not affect equilibrium.

If a reaction causes number of gaseous molecules \uparrow , K \downarrow as P \uparrow at constant T. (products \downarrow , reactants \uparrow)

If a reaction involves only solids and liquids, the effect of pressure on equilibrium is small.

If inert gas is added to an equilibrium mixture of gases at constant T and V, there is no effect on equilibrium.

Adding inert gas at constant T and P has the same effect as lowering the pressure.

For gaseous reactions in which $\Delta v \neq 0$, increase in total pressure shifts equilibrium composition toward the side containing fewer gas moles, but does <u>not</u> change the value of K.

Example:

$$CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$$

 $\mathbf{K} = a_{\mathrm{CO2}} \approx \mathbf{P}_{\mathrm{CO2}}$

<u>Note</u>: activities (or concentrations) of pure solids and liquids do not appear in equilibrium constant expressions because activities of these components = 1, by definition.





Figure 6B.2 The pressure dependence of the degree of dissociation, α , at equilibrium for an $\underline{A(g)} \rightleftharpoons 2 \underline{B(g)}$ reaction for different values of the equilibrium constant *K*. The value $\alpha = 0$ corresponds to pure A; $\alpha = 1$ corresponds to pure B

• Effect of Temperature

Exothermic Reaction: Increase in T favors reactants: Reactants \rightarrow Products + Heat

Endothermic reaction: Increase in T favors product: Reactants + Heat \rightarrow Products

Quantify with van't Hoff equation:

$$\ln K_2 = \ln K_1 - \frac{\Delta_{rxn} H^{\theta}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$



Figure 6B.3 The effect of temperature on a chemical equilibrium can be interpreted in terms of the change in the Boltzmann distribution with temperature and the effect of that change in the population of the species. (a) In an endothermic reaction, the population of B increases at the expense of A as the temperature is raised. (b) In an exothermic reaction, the opposite happens.

Predict the effect of the following on the equilibrium composition of each reaction:

a) increasing the P of: $H_2O(\ell) + CO(g) \xrightarrow{\rightarrow} CO_2(g) + H_2(g)$

- b) increasing the T of: $CH_4(g) + 2F_2(g) \xrightarrow{\rightarrow} CF_4(g) + 2H_2(g)$ [for which $\Delta_f H(CH_4) = -74.81 \text{ kJ/mol and } \Delta_f H(CF_4) = -925 \text{ kJ/mol}$]
- c) adding He at constant T, P to: $(CH_3)_3 CCH_2 Cl(g) \stackrel{\rightarrow}{\leftarrow} (CH_3)_2 C = CHCH_3(g) + HCl(g)$
- d) adding He at constant T,V to reaction (c)
- A) Shift toward products
- B) Shift toward reactants
- C) No change

Temperature Dependence of K

Method 1:

• K(25 °C) $\Delta_{rxn}G^{\theta}$ using $\Delta G = \Delta H - T\Delta S$ $K_a = \exp\left|-\frac{\Delta_{rxn}G^{\theta}}{RT}\right|$

$$K_a = \exp\left[\frac{\Delta_{rxn}S^{\theta}}{R}\right] \exp\left[\frac{-\Delta_{rxn}H^{\theta}}{RT}\right]$$

H and S also depend on T, but not as much as G
So, can assume H and S are ~independent of T

Method 2: • Another approach begins with: $\begin{bmatrix} \partial (G/T) \\ \partial (1/T) \end{bmatrix}_{D} = H$ Gibbs-Helmholtz Equation

- This is applied to each term of definition of ΔG^{θ} giving:
- Substitute $\Delta G^{\theta}/T = -R \ln K$

$$\frac{d}{d(\frac{1}{T})}\frac{\Delta_{rxn}G^{\theta}}{T} = \frac{d}{d(\frac{1}{T})}\sum_{i}v_{i}\frac{\mu_{i}}{T} = \sum_{i}v_{i}H_{m,i}^{\theta} = \Delta_{rxn}H^{\theta}$$

$$\frac{d\ln K_a}{d(V_T)} = -\frac{\Delta_{rxn}H^{\theta}}{R} \qquad \text{or}$$

$$\frac{d\ln K_a}{dT} = \frac{\Delta_{rxn}H^{\theta}}{RT^2}$$

to get van't Hoff equation

More Methods Using van't Hoff Equation

2. If constant H, can integrate
$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta_{rxn} H^{\theta}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \rightarrow \ln K_2 = \ln K_1 - \frac{\Delta_{rxn} H^{\theta}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

3. If H is not constant, get formula for $\Delta_{rxn} H^{\theta}$ from $\Delta_{rxn} H^{\theta} = \Delta_{rxn} H_{ref}^{\theta} + \int_{T_{ref}}^{T} \Delta_{rxn} C_p dT$
 $\frac{d\ln K_a}{dT} = \frac{\Delta_{rxn} H^{\theta}}{RT^2} \ln K_a = \frac{-\Delta_{rxn} G_{ref}^{\theta}}{RT_{ref}} + \int_{T_{ref}}^{T} \frac{\Delta_{rxn} H^{\theta}}{RT^2} dT$ Simplest if you assume Cp is
constant
For the dissociation of chlorine, $Cl_2 \rightleftharpoons 2Cl$
 $\Delta_{rxn} H^{\theta} = 2 \times 121.769 - 0 = 243.538kJ$
 $\Delta_{rxn} G^{\theta} = 2 \times 105.68 - 0 = 211.36kJ$
 $\Delta_{rxn} S^{\theta} = 2 \times 165.198 - 223.066 = 107.330 J/K$
 $\Delta_{rxn} C_{\rho}^{\theta} = 2 \times 21.84 - 33.907 = 9.773 J/K$ Constant Cp:
 $\Delta_{rxn} H = 243538 + 9.773(T - 298.15) = 240624 + 9.773T$
 $\ln K_a = -\frac{211630}{8.31451 \cdot 298.15} + \int_{298.15}^{T} \left[\frac{240624}{RT^2} + \frac{9.773}{RT} \right] dT$

$N_2O_4(g) = 2NO_2(g)$; K = 0.15 at 298 K. What is K at 291 K?

	$N_2O_4(g)$	$NO_2(g)$
$\Delta_{\rm f} {\sf H}^{ heta}$ (kJ/mol)	9.16	33.18
$\Delta_{\mathrm{f}}G^{\mathrm{ heta}}$ (kJ/mol)	97.89	51.31
S_m^{θ} (J/Kmol)	304.29	240.06
C _{pm} ^θ (J/Kmol)	77.28	37.20

$$\Delta_r H^\circ = 2(33.18) - 9.16 = 57.2 \text{ kJ/mol}$$

$$\ln K(T_2) = \ln K(T_1) - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= \ln K(291) = \ln (0.15) - \frac{57200}{8.314} \left(\frac{1}{291} - \frac{1}{298}\right)$$

$$= 2.45$$

K(291) = 0.09

Reminders & Re-cap

- Can use extent of reaction to determine equilibrium concentrations of reactants, products.
- Can write K in terms of molalities or molarities, as well as pressures.
- K depends on enthalpy and entropy factors

• Van't Hoff Eq.:
$$\frac{dlnK_a}{d(1/T)} = -\frac{\Delta_{rxn}H}{R}$$

• Very similar to Clausius-Clapyeron Eq.:

$$\frac{\mathrm{d}lnP}{d(^{1}/_{T})} = -\frac{\Delta_{vap}H}{R}$$

Property	Equation	Property	Equation	
Reaction Gibbs energy	$\Delta_{\mathbf{r}}G = (\partial G/\partial\xi)_{p,T}$	van 't Hoff equation	$\mathrm{d}\ln K/\mathrm{d}T = \Delta_{\mathrm{r}}H^{\ominus}/RT^2$	
Reaction Gibbs energy	$\Delta_{\rm r}G = \Delta_{\rm r}G^{\ominus} + RT\ln Q$	Temperature	$d \ln K / d(1/T) = -\Delta_r H^{\Theta} / R$ $\ln K_0 - \ln K_0$	
Standard reaction Gibbs energy	$\Delta_{\mathbf{r}} G^{\ominus}$ $= \sum \nu \Delta_{\mathbf{f}} G^{\ominus} - \sum \nu \Delta_{\mathbf{f}} G^{\ominus}$	dependence of equilibrium constant	$= -(\Delta_{\rm r} H^{\ominus}/R)(1/T_2 - 1/T_2)$	
	Products Reactants $= \sum_{J} \nu_{J} \Delta_{f} G^{\ominus}(J)$			
Reaction quotient	$Q = \prod_{J} a_{J}^{\nu_{J}}$			
Thermodynamic equilibrium constant	$K = \left(\prod_{J} a_{J}^{\nu_{J}}\right)_{\text{equilibrium}}$			
Equilibrium constant	$\Delta_{\rm r}G^{\ominus} = -RT\ln K$			
Relation between K and K _c	$K = K_c (c^{\Theta} RT/p^{\Theta})^{\Delta v}$			