Chemical Equilibrium

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Chemical Reactions

- Chemical reactions involve an exchange of atoms due to collisions between molecules/atoms.
- An example:

$$CO + \frac{1}{2}O_2 \leftrightarrow CO_2$$

- A common question would be what are the relative amounts of CO and CO_2 at equilibrium.

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Chemical Equilibrium

- The equilibrium composition of a chemically reacting mixture is that which maximizes or minimizes the appropriate Fundamental Relation.
- For most problems of interest, we seek the composition at a given temperature and pressure.
- Thus, Gibbs Function is the appropriate FR.

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The Gibb's Function

- The Gibb's function is

$$G \equiv H - TS$$

$$\bar{g}_i = \bar{h}_i - T\bar{s}_i$$

- It is useful to write it as

$$\bar{g}_{i,T} = \bar{g}^0_{i,T} + R_u T \ln(p_i / p_{ref})$$

- where $\bar{g}^0_{i,T}$ is the Gibbs function of the pure substance at the standard-state pressure and given T.

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The Gibb's Function

- The Gibb's function can be written as

$$\bar{g}^0_{i,T} = \left(\bar{g}^0_{f,i}\right)_{T_{ref}} + \left[\bar{g}^0_i(T) - \bar{g}^0_i(T_{ref})\right]$$

- where $\bar{g}^0_{f,i}$ is the Gibbs function of formation at a reference temperature.
- Like the enthalpy of formation it is zero for elements in their naturally occurring states at the reference condition.
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The Equilibrium Condition

- The equilibrium condition is $dG_{mix} = 0$
- where

$$G_{mix} = \sum_i N_i \overline{g}_{i,T} = \sum_i N_i [\overline{g}^0_{i,T} + R_u T \ln(P_i / P_{ref})]$$

- Therefore,

$$dG_{mix} = 0 = \sum_i dN_i [\overline{g}^0_{i,T} + R_u T \ln(P_i / P_{ref})]$$

- and the sum is thus zero.

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Stoichiometric Relation

- Writing the reaction $CO + \frac{1}{2}O_2 \leftrightarrow CO_2$

is really a statement of conservation of atoms.

- There is one carbon and two oxygen atoms on each side.
- The coefficients 1 and ½ on the left and 1 on the right are called the stoichiometric coefficients.

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Stoichiometric Relation

- More generally, we could write

$$aA + bB + \cdots \Leftrightarrow eE + fF + \cdots$$

- The change in the number of moles of each species is directly proportional to its stoichiometric coefficient times a progress of reaction variable alpha.

$$\begin{aligned} dN_A &= -\alpha a \\ dN_B &= -\alpha b \\ &\vdots \\ dN_E &= +\alpha e \\ dN_F &= +\alpha f \\ &\vdots \end{aligned}$$

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Minimize G

- If we substitute this into the equation for dG_{mix} we obtain

$$\Delta G_T^0 = -R_u T \ln K_p$$

- where

$$\Delta G_T^0 \equiv (e\bar{g}_{E,T}^0 + f\bar{g}_{F,T}^0 + \cdots - a\bar{g}_{A,T}^0 - b\bar{g}_{B,T}^0 - \cdots)_{T_{ref}=T}$$

- and

$$K_p = \frac{(P_E / P_{ref})^e (P_F / P_{ref})^f etc}{(P_A / P_{ref})^a (P_B / P_{ref})^b etc}$$

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The Pressure Based Equilibrium Constant

- K_p is the equilibrium constant
- For example: $CO + \frac{1}{2}O_2 \leftrightarrow CO_2$
- Then $K_P = \frac{(P_{CO_2}/P_{ref})}{(P_{CO}/P_{ref})(P_{O_2}/P_{ref})^{1/2}}$

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The Concentration Based Equilibrium Constant

- The equilibrium relation can be converted from partial pressures to concentrations.
- The molar concentration, represented by square brackets [], can be written in terms of mole fractions as

$$[X_i] = x_i P / R_u T = P_i / R_u T$$

- so we can define an equilibrium constant based on molar concentrations:

$$K_p = K_c (R_u T / P_{ref})^{e+f+\cdots-a-b\cdots}$$

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The Concentration Based Equilibrium Constant

- Which can be written more generally

$$K_p = K_c (R_u T / P_{ref})^{\sum \nu'' - \sum \nu'}$$

- where the v's are the stoichiometric coefficients, or

$$K_c = \frac{[E]^e [F]^f \, etc}{[A]^a [B]^b \, etc} = \frac{\prod_{Prod} [X_i]^{\nu_i''}}{\prod_{Reac} [X_i]^{\nu_i'}}$$

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Equilibrium Constant Data

- Equilibrium constants are tabulated in a number of sources, in particular in the NIST database: janaf.nist.gov

Carbon Dioxide (CO_2) $C_1O_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1}\ mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	-9.364	-393.151	-393.151	INFINITE
100	29.208	179.009	243.568	-6.456	-393.208	-393.683	205.639
200	32.359	199.975	217.046	-3.414	-393.404	-394.085	102.924
298.15	37.129	213.795	213.795	0.	-393.522	-394.389	69.095
300	37.221	214.025	213.795	0.069	-393.523	-394.394	68.670
400	41.325	225.314	215.307	4.003	-393.583	-394.675	51.539
500	44.627	234.901	218.290	8.305	-393.666	-394.939	41.259
600	47.321	243.283	221.772	12.907	-393.803	-395.182	34.404
700	49.564	250.750	225.388	17.754	-393.983	-395.398	29.505
800	51.434	257.494	228.986	22.806	-394.188	-395.586	25.829
900	52.999	263.645	232.500	28.030	-394.405	-395.748	22.969
1000	54.308	269.299	235.901	33.397	-394.623	-395.886	20.679

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