Finding Extent of Reaction

Orientation:
In this activity you will build physical intuition surrounding chemical equilibrium principles and equations by studying the oxidation of carbon monoxide (CO). First you will see how the equilibrium constant, Kp can be obtained two different ways and then compare these with tabulated values for ln(Kp). Knowing whether the reaction is exothermic or endothermic reaction helps you predict how the reaction will shift as system temperature is changed. Furthermore, understanding how mole fractions and total pressures appear in the definition of Kp will help you predict how the reaction will shift as species concentrations and system pressures are changed.

Learning Objectives:
1. Understand how equilibrium constants are derived from enthalpies, entropies, and Gibbs energies of reaction.
2. Study how to determine extent of reaction under constant pressure and constant volume conditions.
3. Apply LeChatelier's principle to make statements how equilibrium will shift when different system conditions are changed.

Targeted Skills:
Integrating – combining parts into a new whole
Validating – using alternative methods to test results
Reasoning with theory – explaining data with accepted knowledge

1. Write a balanced reaction for CO oxidation, assuming complete combustion. Label which are products, and which are reactants.

2. After studying the ideal gas data provided in the spreadsheet, explain how to find ΔH for CO oxidation, ΔS for CO oxidation, and ΔG for CO oxidation.

3. Explain how to compute the equilibrium constant, K_p for CO at your assigned temperature. Validate your answer by checking that attached table of equilibrium constants, noting that the K_p is tabulated in logarithmic form. Remember that R is the universal gas constant (8.314 kJ/kmol-k).

4. For an exothermic reaction such as this, how does the value of Kp change with temperature? What is the significance is Kp being less then unity?

5. Write an equation for CO oxidation including a variable for extent of reaction (α).

6. What is the total number of moles present during dissociation?

7. Define a nonlinear algebraic equation can be used to solve for extent of reaction.

8. Forecast how the yield of CO_2 will change under each of the following conditions. Provide a rationale for each of your predictions.

   a) Increase in system temperature
   b) Increase in system pressure
   c) Addition of more CO
   d) Addition of a catalyst

DISSOCIATION REACTION CO + 1/2*O2 <=> CO2

Temp Kelvin	Hco2 MJ/kmol	Hco MJ/kmol	Ho2 MJ/kmol	DeltaH MJ/kmol
298	-394	-111	0	-283
1500	-332	-72	41	-281
2000	-302	-54	59	-278
2500	-271	-36	78	-274
3000	-240	-17	98	-272
3500	-209	2	118	-270

Temp Kelvin	Sco2 MJ/kmol-K	Sco MJ/kmol-K	So2 MJ/kmol-K	DeltaS MJ/kmol-K	
298	214	198	205	-87	<= note kJ
1500	292	248	258	-85	
2000	309	259	269	-85	
2500	323	267	277	-83	
3000	334	274	285	-83	
3500	344	279	291	-81	

Temp Kelvin	Gco2 MJ/kmol	Gco MJ/kmol	Go2 MJ/kmol	DeltaG MJ/kmol	DH-T*DS MJ/kmol
298	-457	-170	-61	-257	-257
1500	-770	-444	-347	-153	-153
2000	-921	-571	-478	-111	-109
2500	-1079	-703	-615	-69	-68
3000	-1243	-838	-755	-28	-25
3500	-1413	-976	-899	13	12

Temp Kelvin	(- DeltaG/RT) from above	ln(Kp) from text	alpha	CO2_actual	CO_actual	O2_actual	DeltaH w/equil
298	103.5	103.8	0	1	0	0	-283
1500	12.2	12.2	0.000363	0.999637	0.000363	0	-221
2000	6.7	6.6	0.015	0.985	0.008	0.004	-185
2500	3.3	3.3	0.13	0.87	0.13	0.07	-112
3000	1.1	1.1	0.44	0.56	0.44	0.22	-12
3500	-0.4	-0.4	0.75	0.25	0.75	0.37	39

Table A.6 *Equilibrium constants*

At a given temperature, the standard (referring here to a pressure of 1 bar) free enthalpy of reaction or Gibbs energy change (ΔG^0) is related to the equilibrium constant (K_p) by

$$\Delta G_T^0 = -R_0 T \ln K_p$$

and the following values of the equilibrium constants have been calculated from the Gibbs energy tabulations in tables A.4 and A.5.

The chemical reactions considered here are presented in the form

$$\Sigma \nu_i A_i = 0$$

where ν_i is the stoichiometric coefficient of the substance A_i.

The partial pressures of the species in equilibrium are found from

$$\ln K_p = \Sigma \nu_i \ln p_i^*$$

where the dimensionless quantity p_i^* is numerically equal to the partial pressure of substance A_i, in units of **bar**.

Reaction number	Valid range: 300–5000 K	Reaction number	Valid range: 300–5000 K
1	$-2H + H_2 = 0$	2	$-2O + O_2 = 0$
3	$-2NO + N_2 + O_2 = 0$	4	$-H_2 - \frac{1}{2}O_2 + H_2O = 0$
5	$-\frac{1}{2}H_2 - OH + H_2O = 0$	6	$-CO - \frac{1}{2}O_2 + CO_2 = 0$
7	$-CO - H_2O + CO_2 + H_2 = 0$		

$\ln K_p$ – bar

	Reaction numbers							
T (K)	1	2	3	4	5	6	7	T (K)
100	511.058	584.208	213.879	284.475	331.098	328.849	44.375	100
200	250.154	285.590	105.451	139.970	162.100	159.694	19.723	200
298.15	**163.990**	**187.014**	**69.785**	**92.206**	**106.332**	**103.762**	**11.556**	**298.15**
300	162.906	185.774	69.337	91.604	105.630	103.058	11.454	300
400	119.151	135.735	51.277	67.320	77.322	74.670	7.350	400
500	92.822	105.639	40.433	52.689	60.291	57.617	4.928	500
600	75.220	85.531	33.199	42.896	48.908	46.244	3.349	600
700	62.612	71.139	28.027	35.875	40.758	38.124	2.249	700
800	53.130	60.326	24.146	30.591	34.632	32.037	1.447	800
900	45.735	51.902	21.126	26.468	29.858	27.308	0.840	900
1000	39.803	45.153	18.709	23.160	26.031	23.528	0.369	1000
1100	34.938	39.623	16.732	20.446	22.895	20.439	−0.007	1100
1200	30.873	35.009	15.083	18.179	20.279	17.869	−0.310	1200
1300	27.426	31.100	13.688	16.258	18.062	15.698	−0.560	1300
1400	24.464	27.746	12.492	14.607	16.160	13.840	−0.767	1400
1500	21.892	24.835	11.455	13.175	14.510	12.232	−0.942	1500
1600	19.637	22.286	10.548	11.919	13.065	10.828	−1.091	1600
1700	17.643	20.035	9.748	10.810	11.790	9.591	−1.219	1700
1800	15.867	18.032	9.036	9.823	10.655	8.494	−1.330	1800
1900	14.275	16.238	8.400	8.940	9.640	7.514	−1.426	1900

(continued)

Table A.6 *Equilibrium constants (continued)*

T (K)	1	2	3	4	5	6	7	*T* (K)
2000	12.840	14.622	7.827	8.143	8.726	6.633	–1.510	2000
2100	11.540	13.160	7.309	7.422	7.899	5.838	–1.584	2100
2200	10.356	11.829	6.838	6.766	7.146	5.117	–1.649	2200
2300	9.273	10.613	6.408	6.167	6.460	4.460	–1.707	2300
2400	8.280	9.498	6.015	5.617	5.830	3.858	–1.759	2400
2500	7.364	8.471	5.653	5.111	5.251	3.306	–1.805	2500
2600	6.518	7.523	5.319	4.644	4.716	2.797	–1.847	2600
2700	5.733	6.645	5.010	4.211	4.221	2.327	–1.884	2700
2800	5.004	5.829	4.723	3.808	3.761	1.891	–1.918	2800
2900	4.324	5.069	4.457	3.433	3.333	1.486	–1.948	2900
3000	3.689	4.359	4.208	3.083	2.934	1.108	–1.975	3000
3100	3.095	3.695	3.976	2.756	2.560	0.756	–2.000	3100
3200	2.537	3.072	3.758	2.449	2.210	0.426	–2.022	3200
3300	2.012	2.487	3.554	2.160	1.881	0.117	–2.043	3300
3400	1.518	1.936	3.363	1.888	1.572	–0.173	–2.061	3400
3500	1.052	1.416	3.182	1.631	1.280	–0.447	–2.078	3500
3600	0.611	0.925	3.012	1.389	1.005	–0.705	–2.093	3600
3700	0.194	0.460	2.851	1.159	0.744	–0.948	–2.107	3700
3800	–0.202	0.020	2.699	0.941	0.497	–1.178	–2.120	3800
3900	–0.577	–0.397	2.555	0.735	0.263	–1.396	–2.131	3900
4000	–0.934	–0.794	2.419	0.538	0.041	–1.603	–2.141	4000
4100	–1.273	–1.172	2.289	0.351	–0.171	–1.799	–2.150	4100
4200	–1.597	–1.532	2.166	0.173	–0.372	–1.986	–2.159	4200
4300	–1.906	–1.875	2.049	0.003	–0.564	–2.163	–2.166	4300
4400	–2.201	–2.202	1.937	–0.159	–0.747	–2.332	–2.173	4400
4500	–2.482	–2.515	1.830	–0.315	–0.922	–2.494	–2.179	4500
4600	–2.752	–2.815	1.729	–0.463	–1.090	–2.648	–2.185	4600
4700	–3.010	–3.101	1.632	–0.606	–1.250	–2.795	–2.189	4700
4800	–3.258	–3.376	1.539	–0.743	–1.403	–2.936	–2.193	4800
4900	–3.496	–3.640	1.450	–0.874	–1.551	–3.071	–2.197	4900
5000	–3.724	–3.893	1.365	–1.000	–1.692	–3.200	–2.200	5000
5500	–4.740	–5.022	0.988	–1.564	–2.322	–3.773	–2.209	5500
6000	–5.586	–5.964	0.678	–2.037	–2.847	–4.247	–2.210	6000
T (K)	1	2	3	4	5	6	7	*T* (K)