

Example Equilibrium Problem: O₂ dissociation

Heat 1 mole of O₂ at 1 atm to 3000 K. How much O₂ dissociates? Repeat for 0.1 atm.

Species to consider: O₂, O

Neglect O₃, which we can add in a more complex analysis, but we'll see it's negligible.

Choose a reaction: O₂ → 2O

Any form of the reaction is ok, as long as we stick with that form throughout the calculation.

Find stoichiometric coefficients: $\nu_{O_2} = -1$ $\nu_O = 2$

Write equations for mole numbers in terms of advancement according to $N_i = N_{i,0} + \nu_i \xi$

$$N_{O_2} = 1 - \xi \quad N_O = 2 \xi \quad N_{\text{Total}} = N = N_{O_2} + N_O = 1 + \xi \quad (1)$$

Write equilibrium constant formulation. Expand by adding ambient pressure. Substitute $P_i/P = N_i/N$

$$K_p = \prod \left(\frac{P_i}{P_{ref}} \right)^{\nu_i} = \frac{P_O^2 P_{ref}}{P_{O_2}^2 P_{O_2}} = \frac{P_O^2 P_{ref}^2}{P^2 P_{ref}^2 P_{O_2}} = \frac{P_O^2 P}{P^2 P_{O_2} P_{ref}} = \frac{N_O^2 N}{N^2 N_{O_2} P_{ref}} = \frac{N_O^2 P}{N N_{O_2} P_{ref}}$$

Substitute in for mole numbers in terms of advancements from (1).

$$K_p = \frac{(2\xi)^2}{(1-\xi)(1+\xi)} \frac{P}{P_{ref}} = \frac{4\xi^2}{1-\xi^2} \frac{P}{P_{ref}}$$

Solving for advancement gives:

$$\xi = \sqrt{\frac{K_p(P_{ref}/P)}{4 + K_p(P_{ref}/P)}} \quad (2)$$

So given K_p , we can get advancement from (2), and then the mole numbers and mole fractions from (1).

To get K_p , we use the expression:

$$K_p = \exp(-\Delta G^\circ / RT) = \exp\left(\left[-\sum \nu_i \mu_i^\circ\right] / RT\right) = \exp\left(\left[-\sum \nu_i (\hat{h}_i - T \hat{s}_i^\circ)\right] / RT\right) \quad (3)$$

For our reaction, the ΔG° term is:

$$\Delta G^\circ = 2(\hat{h}_O - T \hat{s}_O^\circ) - (\hat{h}_{O_2} - T \hat{s}_{O_2}^\circ) \quad (4)$$

We can get enthalpy and entropy from the coefficients in Burcat or other databases. From Burcat, I get:

O	L 1/900	1	0	0	OG	200.000	6000.000	1000.	1	
						2.54363697E+00	-2.73162486E-05	-4.19029520E-09	4.95481845E-12	-4.79553694E-16
						2.92260120E+04	4.92229457E+00	3.16826710E+00	-3.27931884E-03	6.64306396E-06
						-6.12806624E-09	2.11265971E-12	2.91222592E+04	2.05193346E+00	2.99687009E+04
O2	REF ELEMENT	RUS 890	2	0	OG	200.000	6000.000	1000.	1	
						3.66096065E+00	6.56365811E-04	-1.41149627E-07	2.05797935E-11	-1.29913436E-15
						-1.21597718E+03	3.41536279E+00	3.78245636E+00	-2.99673416E-03	9.84730201E-06
						-9.68129509E-09	3.24372837E-12	-1.06394356E+03	3.65767573E+00	0.00000000E+00

Some things to note: The first seven coefficients are for the high range (here 1000 to 6000 K), so that's what we'll use (yellow highlights). Also, the last entry in the last row is not used in the CHEMKIN fits (green highlight) so ignore it if it's provided.

Use the Chemkin equations:

$$\frac{\hat{h}}{R_u T} = \frac{h}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{\hat{s}^\circ}{R_u} = \frac{s^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

For 3000 K, I get:

$$\hat{h}_{\text{O}} = 3.06e5 \text{ J/mol} \quad \hat{s}_{\text{O}}^\circ = 2.10e2 \text{ J/mol} \quad \hat{h}_{\text{O}_2} = 9.81e4 \text{ J/mol} \quad \hat{s}_{\text{O}_2}^\circ = 2.84e2 \text{ J/mol}$$

Which gives me a ΔG° of 1.09e5 J/mol from (4), and a K_p of 0.01282 from (3).

Note that these values are the same for all pressures.

Use (2) to get advancements. For 1 atm, I now get an advancement of .0565 moles, and for 0.1 atm, it's .1762 moles.

Using our equation (1) for mole numbers, I get, for 1 atm:

$$N_{\text{O}} = .1130, N_{\text{O}_2} = .9435, N = 1.0565, X_{\text{O}} = .1070, X_{\text{O}_2} = .8930$$

While for 0.1 atm, I get:

$$N_{\text{O}} = .3524, N_{\text{O}_2} = .8238, N = 1.1762, X_{\text{O}} = .2996, X_{\text{O}_2} = .7004$$