



	25°C 298 K	327°C 600 K	727°C 1000 K
k ($\text{M}^{-1}\text{s}^{-1}$)	3.82×10^{-11}	0.3174	2.64×10^3
K (from ΔG°)	4.65×10^{-13}	7.43×10^{-7}	2.1×10^4
K_{rev}	2.15×10^{12}	1.346×10^6	4.76×10^3

these are wrong!
wrong!

$A = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
 $E_a = 112.55 \text{ kJ mol}^{-1}$
 at 25°C
 $\Delta H^\circ = 114.1 \text{ kJ mol}^{-1}$
 $\Delta S^\circ = 147 \text{ J mol}^{-1} \text{ K}^{-1}$
 $\Delta G^\circ = 70.4 \text{ kJ mol}^{-1}$ (at 25°C)

$\text{rate}_f = k_f [\text{NO}_2]^2$
 $\text{rate}_r = k_r [\text{NO}]^2 [\text{O}_2]$
 ↓ equal equilibrium
 ↓ equal equilibrium

$k_f [\text{NO}_2]^2 = k_r [\text{NO}]^2 [\text{O}_2]$ equilibrium constant
 $\frac{k_f}{k_r} = \frac{[\text{NO}]^2 [\text{O}_2]}{[\text{NO}_2]^2} = K$ equilibrium expression
 or $\frac{k_r}{k_f} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} = K_{\text{rev}}$

Find equilibrium concentrations at 25°C $[\text{NO}_2]_i = 1.0 \text{ M}$

①

	$2\text{NO}_2(\text{g})$	$2\text{NO}(\text{g})$	$\text{O}_2(\text{g})$
I	1.0	0	0
C	$-2x$	$+2x$	$+x$
E	$1.0 - 2x$	$2x$	x

②

$$\frac{[\text{NO}]^2 [\text{O}_2]}{[\text{NO}_2]^2} = K$$

$$\frac{(2x)^2 (x)}{(1.0 - 2x)^2} = 4.65 \times 10^{-13}$$

③ small x approx

$$\frac{(2x)^2 (x)}{1.0} = 4.65 \times 10^{-13}$$

$$4x^3 = 4.65 \times 10^{-13}$$

$$x = \left(\frac{4.65 \times 10^{-13}}{4} \right)^{1/3}$$

$$x = 4.88 \times 10^{-5}$$

Test x (< 5%)

$$\frac{2(4.88 \times 10^{-5})}{1.0} \times 100\% = 0.0097\%$$

$[\text{NO}_2]_{\text{eq}} = 1.0 - 2(4.88 \times 10^{-5})$
 $= 0.99990 \text{ M}$
 $[\text{NO}]_{\text{eq}} = 2(4.88 \times 10^{-5})$
 $= 9.76 \times 10^{-5} \text{ M}$
 $[\text{O}_2]_{\text{eq}} = 4.88 \times 10^{-5} \text{ M}$

④ cubic!

$$\frac{4x^3}{1.0 - 2x - 2x + 4x^2} = 4.65 \times 10^{-13}$$

$$4x^3 = 4.65 \times 10^{-13} (1.0 - 4x + 4x^2)$$

$$4x^3 = 4.65 \times 10^{-13} - 1.86 \times 10^{-12} x + 1.86 \times 10^{-12} x^2$$

$$4x^3 - 1.86 \times 10^{-12} x^2 + 1.86 \times 10^{-12} x - 4.65 \times 10^{-13} = 0$$

$$x = 4.88 \times 10^{-5}$$

Find equilibrium concentrations at 727°C $[\text{NO}_2]_i = 1.0 \text{ M}$

①

	$2\text{NO}_2(\text{g})$	$2\text{NO}(\text{g})$	$\text{O}_2(\text{g})$
I	1.0	0	0
C	$-2x$	$+2x$	$+x$
E	$1.0 - 2x$	$2x$	x

②

$$\frac{[\text{NO}]^2 [\text{O}_2]}{[\text{NO}_2]^2} = K$$

$$\frac{(2x)^2 (x)}{(1.0 - 2x)^2} = 2.1 \times 10^{-4}$$

③ small x approx

$$\frac{(2x)^2 (x)}{1.0} = 2.1 \times 10^{-4}$$

$$4x^3 = 2.1 \times 10^{-4}$$

$$x = 3.74 \times 10^{-2}$$

Test x (< 5%)

$$\frac{2(3.74 \times 10^{-2})}{1.0} \times 100\% = 7.5\%$$

too big!

$[\text{NO}_2]_{\text{eq}} = 1.0 - 2(3.56 \times 10^{-2})$
 $= 0.9288 \text{ M}$
 $[\text{NO}]_{\text{eq}} = 2(3.56 \times 10^{-2})$
 $= 0.0712 \text{ M}$
 $[\text{O}_2]_{\text{eq}} = 0.0356 \text{ M}$

④

$$4x^3 = 2.1 \times 10^{-4} (1.0 - 4x + 4x^2)$$

$$4x^3 = 2.1 \times 10^{-4} - 8.4 \times 10^{-4} x + 8.4 \times 10^{-4} x^2$$

$$4x^3 - 8.4 \times 10^{-4} x^2 + 8.4 \times 10^{-4} x - 2.1 \times 10^{-4} = 0$$

$$x = 3.56 \times 10^{-2}$$