

Equilibrium of smog formation



Pressure dependence



We can write the equilibrium constant:

$$K = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

If there is a constraint on the total pressure then
We must use Dalton's law to calculate the mole
Fractions.

$$P_{\text{N}_2\text{O}_4} = x_{\text{N}_2\text{O}_4} P_{\text{tot}}$$

$$P_{\text{NO}_2} = x_{\text{NO}_2} P_{\text{tot}}$$

Pressure dependence



The equilibrium constant is

$$K = \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} P_{\text{tot}}$$

For a given initial pressure of N_2O_4 we have

| | N_2O_4 | NO_2 | Total |
|---------|----------------------------------|---------------|----------------------------------|
| Initial | $P_{\text{N}_2\text{O}_4}^0$ | 0 | $P_{\text{N}_2\text{O}_4}^0$ |
| Delta | -x | 2x | +x |
| Final | $P_{\text{N}_2\text{O}_4}^0 - x$ | 2x | $P_{\text{N}_2\text{O}_4}^0 + x$ |

To solve a gas phase problem you need to know whether the pressure can change or not. If it is fixed, then P_{tot} has a value that does not change. The mole fractions are,

$$x_{\text{NO}_2} = \frac{2x}{P_{\text{N}_2\text{O}_4}^0 + x} \quad x_{\text{N}_2\text{O}_4} = \frac{P_{\text{N}_2\text{O}_4}^0 - x}{P_{\text{N}_2\text{O}_4}^0 + x}$$

For example, if we assume that the initial pressure is maintained, then the above values should be substituted into the equilibrium constant

$$K = \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} P_{\text{tot}}$$

$$K = \frac{\left(\frac{2x}{P_{N_2O_4}^0 + x} \right)^2}{\frac{P_{N_2O_4}^0 - x}{P_{N_2O_4}^0 + x}} P_{N_2O_4}^0$$



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$$K = \frac{P_{N_2O_4}^0 (2x)^2}{(P_{N_2O_4}^0 - x)(P_{N_2O_4}^0 + x)}$$

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$$K = \frac{P_{N_2O_4}^0 (2x)^2}{(P_{N_2O_4}^0 - x)(P_{N_2O_4}^0 + x)}$$

$$K(P_{N_2O_4}^0)^2 - (K + 4P_{N_2O_4}^0)x^2 = 0$$

$$x = \sqrt{\frac{K(P_{N_2O_4}^0)^2}{(K + 4P_{N_2O_4}^0)}}$$