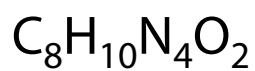
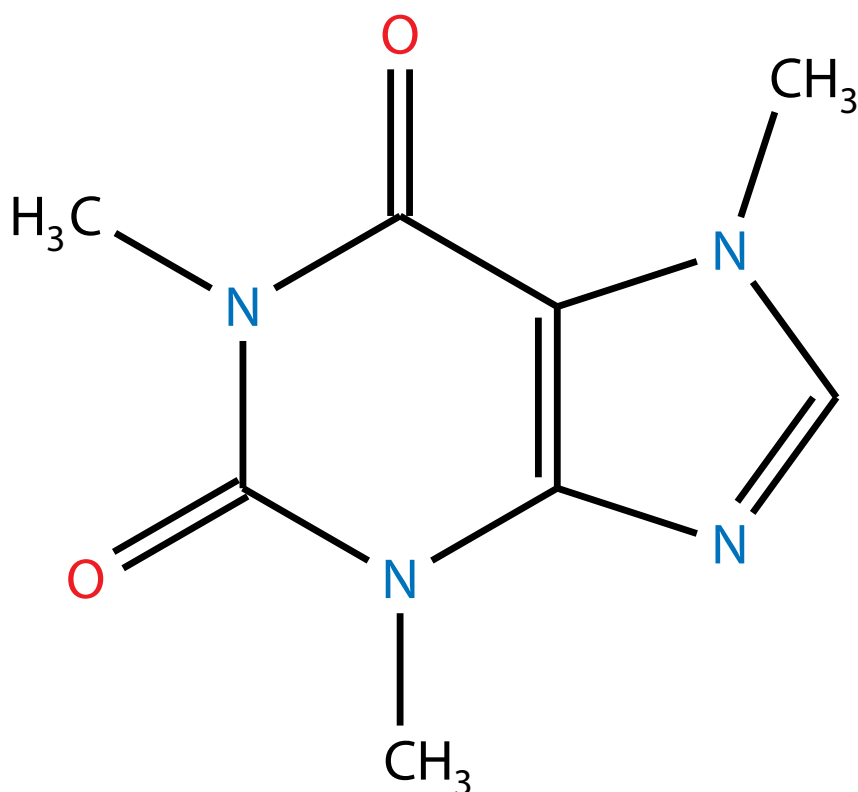


Appendix



1,3,7-trimethylpurine-2,6-dione

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Caffeine

Chapters 8 to 12, 15 to 18

Contents

A. Derivations

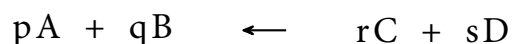
1.	Equilibrium Constant	1
1.1	Elementary Equilibrium	1
1.2	Non-Elementary Equilibrium	3

Derivations

This appendix section details the derivations of various formulas that have appeared in the main body.

1 Equilibrium Constant

For a given equation:



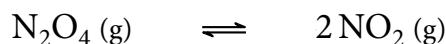
The equilibrium constant is defined as such:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Recall that the system reaches a position of equilibrium when the forward and backward rates of reaction are equal. There are two scenarios to consider in this case — when the given equilibrium reaction is an elementary step, and when it is not.

1.1 Elementary Equilibrium

The equilibrium of N_2O_4 and NO_2 will be studied as an example in this section.



If the main reaction is an elementary reaction, it implies that both the forward and the backward reactions are elementary. Hence, there are two rate constants — one for the forward reaction, k_{fwd} , and one for the reverse k_{rev} .

$$R_{fwd} = k_{fwd}[N_2O_4] \qquad R_{rev} = k_{rev}[NO_2]^2$$

Since both reactions are elementary, the orders of reaction correspond to the stoichiometric coefficients.

Further recall that the equilibrium constant reflects the position of equilibrium of the system (in fixed conditions) — if its magnitude is large, the equilibrium favours the forward reaction, and vice versa.

Thus, the following relationship can be applied:

$$K_c = \frac{k_{fwd}}{k_{rev}}$$

The following equation can be found by slightly rearranging the two rate equations above and appropriately substituting:

$$K_c = \frac{k_{fwd}}{k_{rev}} = \frac{R_{fwd}}{[N_2O_4]} / \frac{R_{rev}}{[NO_2]^2}$$

Since the forward and reverse rates of reaction are the same, they can be cancelled, getting the definition of the equilibrium constant:

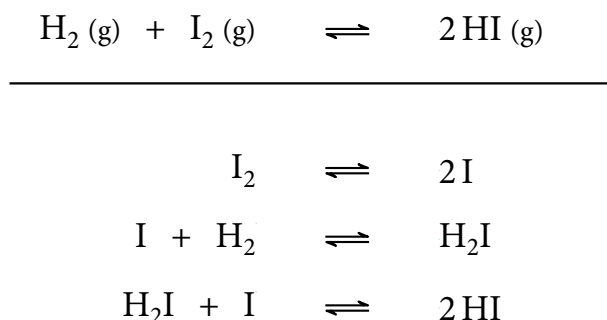
$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

This also indirectly explains why the equilibrium constant takes the product concentrations over the reactant concentrations, instead of the other way around.

1.2 Non-Elementary Equilibrium

Even if the equilibrium itself is not elementary, the original definition of K_c still applies — there are simply more substitution steps to get to it.

Taking the following equilibrium, along with its 3 constituent steps:



The steps have the following equilibrium constants, along with the overall equilibrium constant:

$$K_1 = \frac{[\text{I}]^2}{[\text{I}_2]} \quad K_2 = \frac{[\text{H}_2\text{I}]}{[\text{I}][\text{H}_2]} \quad K_3 = \frac{[\text{HI}]^2}{[\text{I}][\text{H}_2\text{I}]} \quad K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Working backwards from the final equation, a number of substitutions can be performed:

$$\begin{aligned}
 K_c &= \frac{[\text{HI}]^2}{[\text{I}_2][\text{H}_2]} && \Leftarrow [\text{HI}]^2 = K_3[\text{I}][\text{H}_2\text{I}] \\
 &= \frac{K_3[\text{I}][\text{H}_2\text{I}]}{[\text{I}_2][\text{H}_2]} && \Leftarrow [\text{H}_2\text{I}] = K_2[\text{I}][\text{H}_2] \\
 &= \frac{K_3K_2[\text{I}]^2}{[\text{I}_2]} && \Leftarrow [\text{I}]^2 = K_1[\text{I}_2] \\
 &= \frac{K_3K_2K_1[\text{I}_2]}{[\text{I}_2]} = K_1K_2K_3 \\
 K_1K_2K_3 &= \frac{[\text{I}]^2}{[\text{I}_2]} \times \frac{[\text{H}_2\text{I}]}{[\text{I}][\text{H}_2]} \times \frac{[\text{HI}]^2}{[\text{I}][\text{H}_2\text{I}]} = \frac{\cancel{[\text{I}]}}{[\text{I}_2]} \times \frac{1}{\cancel{[\text{I}]}[\text{H}_2]} \times \frac{[\text{HI}]^2}{\cancel{[\text{I}]}[\text{H}_2\text{I}]} \\
 &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K_c
 \end{aligned}$$

Et voila. While this ‘proof’ might seem suspiciously circular, the starting point has to either assume that $K_c = K_1K_2K_3$, or assume that the initial definition of K_c is true. The former theorem can be shown

using the latter, ie. the overall equilibrium constant of a series of sequential equilibria is the product of the individual equilibrium constants.