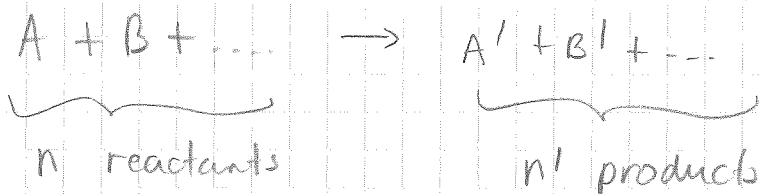


CHEMICAL EQUILIBRIA

Theory:

Reaction



Define Equilibrium constant:

$$K_p = \frac{P_{A'} P_{B'} \dots}{P_A P_B \dots}$$

In equilibrium $N_x \propto \sum e^{-E_i/kT} = Q_x$

$$K_N = \frac{N_{A'} N_{B'} \dots}{N_A N_B \dots} = \frac{Q_{A'} Q_{B'} \dots}{Q_A Q_B \dots} e^{-\Delta E_0^0/kT}$$

\uparrow
 total zero point energy change

\uparrow
 total partition functions referred to lowest energy level of particle

Since $pV = NkT$ we can write

$$K_p = \left(\frac{kT}{V}\right)^{(n'-n)} K_N$$

$$= \left(\frac{kT}{V}\right)^{n'-n} \frac{Q_{A'} Q_{B'} \dots}{Q_A Q_B \dots} e^{-\Delta E_0^0/kT}$$

now write $Q_x = Q_{\text{Trans}} Q_x$ (i.e. separate translation)

\uparrow translation \uparrow internal

$$Q_{\text{Trans}} = \left(\frac{2\pi m_x kT}{h^2}\right)^{3/2} V$$

\uparrow
 volume of box

$$\begin{aligned}
 \text{So } K_p &= \left[\left(\frac{kT}{V} \right) \left(\frac{2\pi kT}{h^2} \right)^{3/2} V \right]^{(n-n')} \\
 &\quad \times \left(\frac{m_{A'} m_{B'} \dots}{m_A m_B \dots} \right)^{3/2} \frac{Q_{A'} Q_{B'} \dots}{Q_A Q_B \dots} e^{-\Delta E_0 / kT} \\
 &\quad \uparrow \qquad \qquad \qquad \uparrow \\
 &\quad \text{this is "reduced mass"} \qquad \text{now internal only} \\
 &= \left[(kT) \left(\frac{2\pi \mu kT}{h^2} \right)^{3/2} \right]^{(n'-n)} \mu^{3/2} \frac{Q_{A'} Q_{B'} \dots}{Q_A Q_B \dots} e^{-\Delta E_0 / kT}
 \end{aligned}$$

So for:

ionisation: $X \rightarrow X^+ + e^- \rightarrow$ SAHA EQUATION

$$\frac{P_{X^+} P_e}{P_X} = kT \left(\frac{2\pi \mu kT}{h^2} \right)^{3/2} \frac{2 Q_{X^+}}{Q_X} e^{-I/kT}$$

↑
ionisation energy.

diatomic dissociation: $AB \rightarrow A + B$

$$K_p^d = \frac{P_A P_B}{P_{AB}} = kT \left(\frac{2\pi \mu kT}{h^2} \right)^{3/2} \frac{Q_A Q_B}{Q_{AB}} e^{-\Delta D_0 / kT}$$

↑
dissociation energy.

So we need $Q_X = Q_{\text{internal}} = Q_{\text{rot}} Q_{\text{vib}} Q_{\text{electronic}} Q_{\text{nuclear}}$
 assume any Q_{nuclear} terms cancel, so

$$Q_X = Q_{\text{rot}} Q_{\text{vib}} Q_{\text{electronic}}$$

$$Q = \sum e^{-E_i / kT}$$

BRIEF HISTORY and MOTIVATION.

1966 First calculations by Tatum for 14 Molecules
- noted importance of errors in ΔD_0

1979 Huber & Herzberg publish large critical compilation of data for thousands of diatomic molecules

1984 Sanval & Tatum calculate for 300 diatomic molecules of astrophysical interest

Polynomials for $T = 1000 - 9000 \text{ K}$

breakdown of ΔD_0 approx
+ no equilibrium

no molecules

Motivation for new calculations:

1) extend to low T for cool stars, planetary environments, etc.

2) data could be improved

IMPROVEMENTS IN NEW CALCULATIONS

for 58 molecules so far

- Not limited to Huber & Herzberg (eg: Si_2)
(use as starting point)
- remove Φ rot approx
- limit for electronic states removed (eg: SiC)
Sauval & Tatum include $E < 40000 \text{ cm}^{-1}$
- extend expansions (eg: H_2^+)

eg.
$$E_{\text{vib}} = hc \left(w_e \left(v + \frac{1}{2} \right) - w_e x_e \left(v + \frac{1}{2} \right)^2 + w_e y_e \left(v + \frac{1}{2} \right)^3 + \dots \right)$$

Sauval and Tatum cut at second term

- some negative ions done properly, eg H_2^-

Sauval & Tatum assume same properties as neutral molecule.

Note: we also need all atomic Φ including negative ions. Use NIST for neutrals and singly ionised atoms.

For negative ions collect from literature.

Luckily often very easy, eg.

$\text{F}^- \rightarrow$ only one state

1s since Ne like $\rightarrow \Phi = 1$

