# Chemical reaction <br> Masatsugu Sei Suzuki <br> Department of Physics, SUNY at Binghamton <br> (Date: October, 14, 2017) 

Equilibrium in reactions
We may write the equation of a chemical reaction as

$$
\sum v_{j} A_{j}=0
$$

where $A_{j}$ denotes the chemical species, and the $v_{j}$ 's are the coefficients of the species in the reaction equation.
((Example))

$$
\begin{aligned}
& \mathrm{H}_{2}+\mathrm{Cl}_{2}=2 \mathrm{HCl} \\
& 1 . \mathrm{H}_{2}+1 \mathrm{Cl}_{2}=2 \mathrm{HCl} \\
& v_{1}=1,
\end{aligned} \quad \mathrm{~A}_{1}=\mathrm{H}_{2}, ~ 子 \begin{array}{ll}
v_{2}=1, & \mathrm{~A}_{2}=\mathrm{Cl}_{2} \\
v_{3}=-2, & \mathrm{~A}_{3}=\mathrm{HCl}
\end{array}
$$

The discussion of the chemical equilibria is usually presented for reactions under conditions of constant pressure and temperature. In equilibrium $G$ is an extremum and dG must be zero.

$$
d G=\sum_{j} \mu_{j} d N_{j}-S d T+V d P
$$

Since $d P=d T=0$,

$$
d G=\sum_{j} \mu_{j} d N_{j}
$$

The change in the Gibbs free energy in reaction depends on the chemical potentials of the reactants. In equilibrium $G$ is an extremum and $\mathrm{d} G$ must be zero

$$
d G=\sum_{j} \mu_{j} d N_{j}=0
$$

We may write $d N_{j}$ in the form

$$
d N_{j}=v_{j} d \hat{N}
$$

where $d \hat{N}$ indicates how many times the reaction takes place

$$
d G=\sum_{j}\left(\mu_{j} v_{j}\right) d \hat{N}=0
$$

In equilibrium, $\quad d G=0$, so that

$$
d G=\sum_{j} \mu_{j} v_{j}=0
$$

## 2. Equilibrium for ideal gases

We obtain a simple and useful form of the general equilibrium condition

$$
\sum_{j} \mu_{j} v_{j}=0
$$

When we assume that each of the constituents acts as an ideal gas. The single molecule energy of the molecule consisting of gas splits into a term representing the translational motion of the molecular center of mass (CM) and another portion that reflects the internal state; rotation, vibration, and spin multiplicity;

$$
Z_{j}=Z_{j}(C M) Z_{j}(\mathrm{int})
$$

use the chemical potential of species $j$ as

$$
\mu_{j}=k_{B} T \ln \left(\frac{n_{j}}{C_{j}}\right)
$$

Note that

$$
C_{j}=n_{Q j}\left[Z_{j}(\text { int }) \exp \left(-\beta E_{j}\right)\right]
$$

where $Z_{j}(C M)$ contributes to the factor, $n_{Q_{j}} \exp \left(-\beta E_{j}\right), E_{j}$ is the energy of the ground state of the translational motion and $Z_{j}(\mathrm{int})$ is the internal partition function. For the spin multiplicity, we have

$$
Z_{j}(\mathrm{int})=2 S+1
$$

where $S$ is the spin. Then the equation $\sum_{j} \mu_{j} v_{j}=0$ can be rearranged as

$$
\sum_{j} v_{j} \ln n_{j}=\sum_{j} v_{j} \ln C_{j}
$$

or

$$
\sum_{j} \ln {n_{j}}^{\mu_{j}}=\sum_{j} \ln C_{j}{ }^{\mu_{j}}
$$

or

$$
n_{1}^{V_{1}} n_{2}^{V_{2}} n_{3}^{V_{3}} n_{4}^{V_{4}} \ldots . .=C_{1}^{V_{1}} C_{2}^{V_{2}} C_{3}^{V_{3}} C_{4}^{V_{4}} \ldots . .=K(T)
$$

where $K(T)$ is called the equilibrium constant, and is a function of $T$. Then

$$
\begin{aligned}
K(T) & =n_{1}{ }^{V_{1}} n_{2}{ }^{v_{2}} n_{3}^{{ }^{V_{3}}} n_{4}^{V_{4}} \ldots . . \\
& =C_{1}^{{ }^{1} 1} C_{2}{ }^{v_{2}} C_{3}^{{ }^{V_{3}}} C_{4}^{{ }^{V_{4}}} \ldots . . \\
& \left.\left.\left.=\left[n_{Q 1}^{{ }^{V_{1}}} n_{Q 2}{ }^{v_{2}} n_{Q 3}{ }^{{ }^{V_{3}}} n_{Q 4}{ }^{V_{4}} \ldots . .\right]\left\{Z_{1}(\mathrm{int})\right]^{v_{1}} Z_{2}(\mathrm{int})\right]^{v_{2}}\left[Z_{3}(\mathrm{int})\right]^{v_{3}} Z_{4}(\mathrm{int})\right]^{v_{4}} \ldots . .\right\} \\
& \exp \left[-\beta\left(v_{1} E_{1}+v_{2} E_{2}+\ldots .\right)\right]
\end{aligned}
$$

where

$$
\ln \left[Z_{j}(\mathrm{int})\right]^{v_{j}}=v_{j} \ln \left[Z_{j}(\mathrm{int})\right]=-\beta v_{j} F_{j}(\mathrm{int})
$$

or

$$
\left[Z_{j}(\mathrm{int})\right]^{\nu_{j}}=\exp \left[-\beta v_{j} F_{j}(\mathrm{int})\right]
$$

where

$$
F_{j}(\mathrm{int})=-k_{B} T \ln \left[Z_{j}(\mathrm{int})\right]
$$

Then we have
or

$$
\begin{aligned}
K(T) & =n_{1}^{v_{1}} n_{2}^{v_{2}} n_{3}^{{ }^{{ }_{3}}} n_{4}^{v_{4}} \ldots . . \\
& =\left(n_{Q 1}{ }^{V_{1}} n_{Q 2}{ }^{v_{2}} n_{Q 3}{ }^{v_{3}} n_{Q 4}{ }^{v_{4}} \ldots . .\right) \exp \left[-\beta\left(v_{1} E_{1}+v_{2} E_{2}+\ldots .\right)\right] \\
& \times \exp \left\{-\beta\left[v_{1} F_{1}(\text { int })+v_{2} F_{2}(\text { int })+\ldots . .\right]\right\}
\end{aligned}
$$

## ((Example))

Chemical reaction:

$$
\begin{aligned}
A & +B-C=0 \quad \text { (reaction) } \\
K & =\frac{[A][B]}{[C]} \\
& \left.=\frac{n_{Q A} n_{Q B}}{n_{Q C}} \exp \left[-\beta\left(E_{A}+E_{B}-E_{C}\right)\right] \times \exp \left\{-\beta\left[F_{A}(\mathrm{int})+F_{B}(\mathrm{int})-F_{C} \mathrm{int}\right)\right]\right\}
\end{aligned}
$$

Suppose that

$$
Z_{j}(\mathrm{int})=2 S+1 \text { with } S=0 . \text { In other words, we have }
$$

$$
F_{j}(\text { int })=-k_{B} T \ln Z_{j}(\text { int })=-k_{B} T \ln (1)=0 .
$$

$$
\begin{aligned}
& K(T)=n_{1}^{V_{1}} n_{2}^{V_{2}} n_{3}^{V_{3}} n_{4}^{V_{4}} \ldots . . \\
& =\left(n_{Q 1}{ }^{v_{1}} n_{Q 2}{ }^{v_{2}} n_{Q 3}{ }^{{ }^{{ }^{3}}} n_{Q 4}{ }^{v_{4}} \ldots . .\right) \exp \left\{-\beta\left[v_{1} F_{1}(\mathrm{int})+v_{2} F_{2}(\mathrm{int})+\ldots . .\right]\right\} \\
& =\left(n_{Q 1}{ }^{v_{1}} n_{Q 2}{ }^{v_{2}} n_{Q 3}{ }^{{ }^{{ }_{3}}} n_{Q 4}{ }^{v_{4}} \ldots . .\right) \exp \left[-\beta\left(v_{1} E_{1}+v_{2} E_{2}+\ldots . .\right)\right] \\
& \times \exp \left\{-\beta\left[\nu_{1} F_{1}(\mathrm{int})+\nu_{2} F_{2}(\mathrm{int})+\ldots . .\right]\right\}
\end{aligned}
$$

$$
\begin{aligned}
& \times \exp \left\{\left[v_{1} \ln Z_{1}(\mathrm{int})+\nu_{2} \ln Z_{2}(\mathrm{int})+\ldots . .\right]\right\}
\end{aligned}
$$

$$
\begin{aligned}
& \times\left[Z_{1}(\mathrm{int})^{\nu_{1}} Z_{2}(\mathrm{int})^{v_{2}} \ldots . .\right]
\end{aligned}
$$

Then we have

$$
K=\frac{[A \llbracket[B]}{[C]}=\frac{n_{Q A} n_{Q B}}{n_{Q C}} \exp (-\beta \Delta H)
$$

where

$$
E_{A}+E_{B}-E_{C}=\Delta H
$$



Schematic coordinate
$[\mathrm{A}],[\mathrm{B}]$, and $[\mathrm{C}]$ denote the concentration of $\mathrm{A}, \mathrm{B}$, and C . The energy $\Delta$ measures the energy involved in the reaction and determine the equilibrium concentration ratio,

$$
\frac{[A][B]}{[C]} .
$$

The activation energy is the height of the potential barrier to be negotiated before the reaction can proceed, and it determines the rate at which the reaction takes place.

## 3. Problem and Solution (1)

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980).

Problem 9-2
2. Thermal ionization of hydrogen. Consider the formation of atomic hydrogen in the reaction $\mathrm{e}+\mathrm{H}^{+} \leftrightharpoons \mathrm{H}$, where e is an electron, as the adsorption of an electron on a proton $\mathrm{H}^{+}$. (a) Show that the equilibrium concentrations of the reactants satisfy the relation

$$
\begin{equation*}
[\mathrm{e}]\left[\mathrm{H}^{+}\right] /[\mathrm{H}] \cong n_{Q} \exp (-I / \tau) \tag{47}
\end{equation*}
$$

where $I$ is the energy required to ionize atomic hydrogen, and $n_{Q} \equiv\left(m \tau / 2 \pi \hbar^{2}\right)^{3 / 2}$ refers to the electron. Neglect the spins of the particles; this assumption does not affect the final result. The result is known as the Saha equation. If all the electrons and protons arise from the ionization of hydrogen atoms, then the concentration of protons is equal to that of the electrons, and the electron concentration is given by

$$
\begin{equation*}
[\mathrm{e}]=[\mathrm{H}]^{1 / 2} n_{Q}{ }^{1 / 2} \exp (-I / 2 \tau) . \tag{48}
\end{equation*}
$$

A similar problem arises in semiconductor physics in connection with the thermal ionization of impurity atoms that are donors of electrons.

Notice that:
(1) The exponent involves $\frac{1}{2} I$ and not $I$, which shows that this is not a simple "Boltzmann factor" problem. Here $I$ is the ionization energy.
(2) The electron concentration is proportional to the square root of the hydrogen atom concentration.
(3) If we add excess electrons to the system, then the concentration of protons will decrease.
(b) Let $[\mathrm{H}(\mathrm{exc})]$ denote the equilibrium concentration of H atoms in the first excited electronic state, which is $\frac{3}{4} I$ above the ground state. Compare $[\mathrm{H}(\mathrm{exc})]$ with $[\mathrm{e}]$ for conditions at the surface of the Sun, with $[\mathrm{H}] \simeq 10^{23} \mathrm{~cm}^{-3}$ and $T \simeq 5000 \mathrm{~K}$.
(Solution))
(a)

Thermal ionization of hydrogen

$$
e^{-}+H^{+}=H
$$

The law of mass action:

$$
\frac{\left[e^{-}\right]\left[H^{+}\right]}{[H]}=\frac{n_{Q} n_{Q H}^{+}}{n_{Q H}} \exp \left[-\beta\left(E_{e}+E_{H^{+}}-E_{H}\right)\right]
$$

Here we define the ionization energy

$$
I=E_{e}+E_{H^{+}}-E_{H} .
$$

Note that

$$
\begin{aligned}
& n_{Q H}=n_{Q H^{+}} \\
& \frac{\left[e^{-}\right]\left[H^{+}\right]}{[H]}=n_{Q} \exp (-\beta I)
\end{aligned}
$$

with

$$
n_{Q}=\left(\frac{m k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}
$$

If all the electrons and protons arise from the ionization from hydrogen atoms; $\left[e^{-}\right]=\left[H^{+}\right]$, then we get

$$
\left[e^{-}\right]^{2}=[H] n_{Q} \exp (-\beta I)
$$

or

$$
\left[e^{-}\right]=[H]^{1 / 2} n_{Q}^{1 / 2} \exp \left(-\frac{\beta I}{2}\right)
$$

where

$$
\begin{aligned}
& {[H]=10^{23}, \quad I=13.6 \mathrm{eV} . \quad T=5000 \mathrm{~K} .} \\
& n_{Q}=\left(\frac{m k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}=8.53721 \times 10^{20} \mathrm{~cm}^{-3}
\end{aligned}
$$

$$
\begin{aligned}
& \frac{I}{k_{B} T}=31.5643 \\
& {\left[e^{-}\right]=1.29291 \times 10^{15} \mathrm{~cm}^{-3}}
\end{aligned}
$$

(b) $[H(e x c)]$ denotes the equilibrium concentration of H atoms in the first excited electronic state

$$
[H(e x c)]=4[H] \exp \left[-\beta \frac{3 I}{4}\right]=4 \times 5.23436 \times 10^{12} \mathrm{~cm}^{-3}=2.0937 \times 10^{13} \mathrm{~cm}^{-3}
$$

The factor 4 is needed. Note that the first excited state is $n=2$. Since $l=1$ ( 3 states; d-orbitals) and $l=0$ ( 1 state; s-orbital). It is four-fold degenerate.

## ((Mathematica))

## Clear["Global`*"];

$$
\begin{aligned}
& \text { rule1 }=\left\{k B \rightarrow 1.3806504 \times 10^{-16}, N A \rightarrow 6.02214179 \times 10^{23},\right. \\
& \mathrm{c} \rightarrow 2.99792 \times 10^{10}, \hbar \rightarrow 1.05457162810^{-27}, \mathrm{me} \rightarrow 9.1093821510^{-28}, \\
& \mathrm{qe} \rightarrow 4.8032068 \times 10^{-10}, \mathrm{eV} \rightarrow 1.602176487 \times 10^{-12}, \\
& \mathrm{I} 1\left.\rightarrow 13.6 \mathrm{eV}, \mathrm{~T} 1 \rightarrow 5000, \mathrm{NH} \rightarrow 10^{23}\right\} ;
\end{aligned}
$$

$$
\mathrm{nQ}=\left(\frac{\mathrm{me} k B T 1}{2 \pi \hbar^{2}}\right)^{3 / 2} / / . \text { rule1 }
$$

$8.53721 \times 10^{2 \theta}$

I1 / / . rule1
kB T1
31.5643
$\mathrm{Ne}=\mathrm{NH}^{1 / 2} \mathrm{nQ}^{1 / 2} \operatorname{Exp}\left[-\frac{\mathrm{I} 1}{2 \mathrm{kB} \text { T1 }}\right] / /$. rule1
$1.29291 \times 10^{15}$
$4 \mathrm{NH} \operatorname{Exp}\left[-\frac{3 \mathrm{I} 1}{4 \mathrm{kB} \mathrm{T1}}\right] / /$. rule1
$2.09375 \times 10^{13}$

## 4. Problem and Solution (2)

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980).

Problem 9-3
3. Ionization of donor impurities in semiconductors. A pentavalent impurity (called a donor) introduced in place of a tetravalent silicon atom in crystalline silicon acts like a hydrogen atom in free space, but with $e^{2} / \epsilon$ playing the role of $e^{2}$ and an effective mass $m^{*}$ playing the role of the electron mass $m$ in the description of the ionization energy and radius of the ground state of the impurity atom, and also for the free electron. For silicon the dielectric constant $\epsilon=11.7$ and, approximately, $m^{*}=0.3 \mathrm{~m}$. If there are $10^{17}$ donors per $\mathrm{cm}^{3}$, estimate the concentration of conduction electrons at 100 K .
((Solution))
Energy separation between the donor level and the conduction band $\Delta$ is

$$
\Delta=\frac{1}{\varepsilon}\left(\frac{m^{*}}{m}\right) 13.56 \mathrm{eV}
$$

For $\quad$ Si, $\frac{m^{*}}{m}=0.3, \quad \varepsilon=11.7$.

$$
\Delta=0.0297 \mathrm{eV}
$$

The law of mass action:


$$
\begin{aligned}
\frac{\left[D^{+}\right]\left[e^{-}\right]}{[D]} & =\frac{n_{Q}\left(D^{+}\right) n_{Q}}{n_{Q}(D)} \exp \left[-\beta\left(E_{D^{+}}+E_{e}-E_{D}\right)\right] \\
& =\frac{n_{Q}\left(D^{+}\right) n_{Q}}{n_{Q}(D)} \exp (-\beta \Delta)
\end{aligned}
$$

Here we use the relation $\quad n_{Q}(D)=n_{Q}\left(D^{+}\right)$

$$
n_{Q}=\left(\frac{2 \pi m k_{B} T}{h^{2}}\right)^{3 / 2}=\left(\frac{m k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}
$$

We use

$$
\begin{aligned}
& {\left[D^{+}\right]=n_{e} \quad\left[e^{-}\right]=n_{e}, \quad[D]=n_{d}-n_{e} .} \\
& T=300 \mathrm{~K}, \quad n_{d}=10^{17} . \\
& n_{Q}=\left(\frac{m k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}=2.41469 \times 10^{18} \mathrm{~cm}^{-3}
\end{aligned}
$$

We have the equation to determine the value of $n_{e}$.

$$
\frac{n_{e}^{2}}{n_{d}-n_{e}}=n_{Q} \exp (-\beta \Delta)=7.69216 \times 10^{16}
$$

and get the value

$$
n_{e}=5.73066 \times 10^{16} \mathrm{~cm}^{-3} .
$$

## ((Mathematica))

## Clear["Global`*"];

rule1 $=\left\{k B \rightarrow 1.3806504 \times 10^{-16}, N A \rightarrow 6.02214179 \times 10^{23}\right.$,
$c \rightarrow 2.99792 \times 10^{10}, \hbar \rightarrow 1.05457162810^{-27}$, me $\rightarrow 9.1093821510^{-28}$,
qe $\rightarrow 4.8032068 \times 10^{-10}, e V \rightarrow 1.602176487 \times 10^{-12}$,
I1 $\left.\rightarrow 13.6 \mathrm{eV}, \mathrm{T} 1 \rightarrow 100, \Delta \rightarrow 0.0297 \mathrm{eV}, \mathrm{nd} \rightarrow 10^{17}\right\}$;
$n Q=\left(\frac{m e k B T 1}{2 \pi \hbar^{2}}\right)^{3 / 2} / /$. rule1
$2.41469 \times 10^{18}$
$\mathrm{s} 1=\mathrm{nQ} \operatorname{Exp}\left[\frac{-\Delta}{\mathrm{kB} \mathrm{T1}}\right] / /$. rule1
$7.69216 \times 10^{16}$
eq1 $=\frac{n e^{2}}{n d-n e}==s 1 / /$. rule1 //Simplify
$\frac{7.69216 \times 10^{33}-7.69216 \times 10^{16} \mathrm{ne}-1 . \mathrm{ne}^{2}}{1 . \times 10^{17}-1 . \text { ne }}=0$

Solve[eq1, ne] // Simplify[\#, ne > 0] \&
*.- Solve: Solve was unable to solve the system with inexact coefficients. The answer was obtained by solving a corresponding exact system and numericizing the result.
$\left\{\left\{n e \rightarrow-1.34228 \times 10^{17}\right\}, \quad\left\{n e \rightarrow 5.73066 \times 10^{16}\right\}\right\}$
5. Problem and Solution (3)
C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980). Problem 9-4
4. Biopolymer growth. Consider the chemical equilibrium of a solution of linear polymers made up of identical units. The basic reaction step is monomer $+N$ mer $=(N+1)$ mer. Let $K_{N}$ denote the equilibrium constant for
this reaction. (a) Show from the law of mass action that the concentrations [ $\cdots$ ] satisfy

$$
\begin{equation*}
[N+1]=[1]^{N+1} / K_{1} K_{2} K_{3} \cdots K_{N} \tag{49}
\end{equation*}
$$

(b) Show from the theory of reactions that for ideal gas conditions (an ideal solution):

$$
\begin{equation*}
K_{N}=\frac{n_{Q}(N) n_{Q}(1)}{n_{Q}(N+1)} \exp \left[\left(F_{N+1}-F_{N}-F_{1}\right) / \tau\right] . \tag{50}
\end{equation*}
$$

Here

$$
\begin{equation*}
n_{Q}(N)=\left(2 \pi \hbar^{2} / M_{N} \tau\right)^{-3 / 2} \tag{51}
\end{equation*}
$$

where $M_{N}$ is the mass of the $N$ mer molecule, and $F_{N}$ is the free energy of one $N$ mer molecule. (c) Assume $N \gg 1$, so that $n_{Q}(N) \simeq n_{Q}(N+1)$. Find the concentration ratio $[N+1] /[N]$ at room temperature if there is zero free energy change in the basic reaction step: that is, if $\Delta \mathrm{F}=F_{N+1}-F_{N}-F_{1}=0$. Assume [1] $=10^{20} \mathrm{~cm}^{-3}$, as for amino acid molecules in a bacterial cell. The molecular weight of the monomer is 200 . (d) Show that for the reaction to go in the direction of long molecules we need $\Delta F<-0.4 \mathrm{eV}$, approximately. This condition is not satisfied in Nature, but an ingenious pathway is followed that simulates the condition. An elementary discussion is given by C. Kittel, Am. J. Phvs. 40.60 (1972).
((Solution))
Monomer:
$N=1$
$N=2$

$N=3$


$$
\begin{aligned}
& \text { Monomer }+N_{\mathrm{mer}}=(N+1)_{\mathrm{mer}} \\
& K_{N}=\frac{[1][N]}{[N+1]}
\end{aligned}
$$

Similarly we have

$$
\begin{aligned}
& K_{N-1}=\frac{[1][N-1]}{[N]} \\
& K_{N-2}=\frac{[1][N-2]}{[N-1]}
\end{aligned}
$$

$$
K_{3}=\frac{[1][3]}{[4]}
$$

$$
K_{2}=\frac{[1][2]}{[3]}
$$

$$
K_{1}=\frac{[1][1]}{[2]}
$$

From these equations, we get

$$
\begin{aligned}
K_{1} K_{2} K_{3} \ldots . . K_{N-2} K_{N-1} K_{N} & =\frac{[1][1]}{[2]} \frac{[1][2]}{[3]} \frac{[1][3]}{[4]} \cdots \ldots . . \frac{[1][N-2]}{[N-1]} \frac{[1][N-1]}{[N]} \frac{[1][N]}{[N+1]} \\
& =\frac{[1]^{N+1}}{[N+1]}
\end{aligned}
$$

Thus we obtain

$$
[N+1]=\frac{[1]^{N+1}}{K_{1} K_{2} K_{3} \ldots . . K_{N-2} K_{N-1} K_{N}}
$$

We consider

$$
K_{N}=\frac{[1][N]}{[N+1]}
$$

From the definition, we have

$$
\begin{aligned}
K_{N} & =\frac{n_{Q}(1) n_{Q}(N)}{n_{Q}(N+1)} \exp \left[\beta\left(F_{N+1}-F_{N}-F_{1}\right)\right] \\
& =\frac{n_{Q}(1) n_{Q}(N)}{n_{Q}(N+1)} \exp (\beta \Delta F)
\end{aligned}
$$

with

$$
\begin{aligned}
& \Delta F=F_{N+1^{1}}-F_{N}-F_{1} \\
& n_{Q}(N)=\left(\frac{M_{N} k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2} .
\end{aligned}
$$

$M_{N}$ is the mass of $N_{m e r}$ molecules and $F_{N}$. is the free energy of one $\mathrm{N} N_{m e r}$ molecule.
(c) Assume $N \gg 1$

$$
n_{Q}(N+1) \approx n_{Q}(N)
$$

Then

$$
K_{N}=n_{Q}(1) \exp \left[-\beta\left(F_{N}+F_{1}-F_{N+1}\right)\right]
$$

The concentration ratio

$$
\begin{aligned}
\frac{[N+1]}{[N]} & =\frac{[1][ }{K_{N}} \\
& =\frac{[1]}{n_{Q}(1)} \exp \left[\beta\left(F_{N}+F_{1}-F_{N+1}\right)\right] \\
& =\frac{[1]}{n_{Q}(1)} \exp (-\beta \Delta F)
\end{aligned}
$$

If $\Delta F=F_{N+1}-F_{N}-F_{1}=0$

$$
\frac{[N+1]}{[N]}=\frac{[1]}{n_{Q}(1)}=[1]\left(\frac{M k_{B} T}{2 \pi \hbar^{2}}\right)^{-3 / 2}
$$

Here we have

$$
[1]=10^{20} \mathrm{~cm}^{-3} . \quad T=300 \mathrm{~K} .
$$

Molecular weight of the monomer 200 g per mol

$$
\begin{aligned}
& M=\frac{200}{N_{A}} \\
& n_{Q}(1)=2.76203 \times 10^{27} \mathrm{~cm}^{-3} \\
& \frac{[N+1]}{[N]}=3.62058 \times 10^{-8}
\end{aligned}
$$

(d)

$$
\frac{[N+1]}{[N]}=\frac{[1]}{n_{Q}(1)} \exp (-\beta \Delta F)
$$

For the reaction to go in the direction of long molecules

$$
\frac{[N+1]}{[N]}>1
$$

or

$$
\ln \frac{[1]}{n_{Q}(1)}>\beta \Delta F
$$

or

$$
\begin{aligned}
& k_{B} T \ln \frac{[1]}{n_{Q}(1)}>\Delta F \\
& \Delta F<-0.44295 \mathrm{eV}
\end{aligned}
$$

6. Problem and Solution (4)
C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980).

Problem 9-5
5. Particle-antiparticle equilibrium. (a) Find a quantitative expression for the thermal equilibrium concentration $n=n^{+}=n^{-}$in the particle-antiparticle reaction $\mathrm{A}^{+}+\mathrm{A}^{-}=0$. The reactants may be electrons and positrons; protons and antiprotons; or electrons and holes in a semiconductor. Let the mass of either particle be $M$; neglect the spins of the particles. The minimum energy release when $\mathrm{A}^{+}$combines with $\mathrm{A}^{-}$is $\Delta$. Take the zero of the energy scale as the energy with no particles present. (b) Estimate $n$ in $\mathrm{cm}^{-3}$ for an electron (or a hole) in a semiconductor $T=300 \mathrm{~K}$ with a $\Delta$ such that $\Delta / \tau=20$. The hole is viewed as the antiparticle to the electron. Assume that the electron concentration is equal to the hole concentration; assume also that the particles are in the classical regime. (c) Correct the result of (a) to let each particle have a spin of $\frac{1}{2}$. Particles that have antiparticles are usually fermions with spins of $\frac{1}{2}$.
((Solution))
(a)

$$
\begin{aligned}
& A^{+}+A^{-}=0 \\
& n^{+} n^{-}=n_{Q+} n_{Q-} \exp \left[-\beta\left(E_{+}+E_{-}-0\right)\right.
\end{aligned}
$$

When

$$
E_{+}+E_{-}=\Delta, \quad n_{Q+}=n_{Q-}=\left(\frac{M k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}
$$

Then we get

$$
n=n^{+}=n^{-}=\left(\frac{M k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2} \exp \left(-\frac{\beta \Delta}{2}\right)
$$

(b) In the semiconductor

$$
\begin{aligned}
& M=m(\text { mass of electron and hole }) \\
& n_{Q}=\left(\frac{m k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}
\end{aligned}
$$

When $\beta \Delta=20, \quad T=300 \mathrm{~K}$

$$
\begin{aligned}
& n_{Q}=1.25471 \times 10^{19} \mathrm{~cm}^{-3} \\
& n=5.69637 \times 10^{14} \mathrm{~cm}^{-3} .
\end{aligned}
$$

When $Z_{\text {int }}=(2 S+1)$,

$$
\begin{aligned}
n^{+} n^{-} & =n_{Q+} n_{Q-} \exp (-\beta \Delta) Z_{1}(\mathrm{int}) Z_{2}(\text { int }) \\
& =(2 S+1)^{2} n_{Q+} n_{Q-} \exp (-\beta \Delta)
\end{aligned}
$$

For $n=n_{+}=n_{-}, \quad n_{Q}=n_{Q_{+}}=n_{Q_{-}}, \quad S=\frac{1}{2}$

$$
n^{2}=(2 S+1)^{2} n_{Q}^{2} \exp (-\beta \Delta)
$$

or

$$
\begin{aligned}
n & =(2 S+1) n_{Q} \exp \left(-\frac{\beta \Delta}{2}\right) \\
& =2 n_{Q} \exp \left(-\frac{\beta \Delta}{2}\right)
\end{aligned}
$$

## ((Mathematica))

Clear["Global`*"];
rule1 $=\left\{k B \rightarrow 1.3806504 \times 10^{-16}, N A \rightarrow 6.02214179 \times 10^{23}\right.$,

$$
c \rightarrow 2.99792 \times 10^{10}, \hbar \rightarrow 1.05457162810^{-27}, \mathrm{me} \rightarrow 9.1093821510^{-28},
$$

$$
\mathrm{qe} \rightarrow 4.8032068 \times 10^{-10}, \mathrm{eV} \rightarrow 1.602176487 \times 10^{-12}
$$

$$
\text { I1 } \rightarrow 13.6 \mathrm{eV}, \mathrm{~T} 1 \rightarrow 300, \beta \Delta \rightarrow 20\} ;
$$

$n Q=\left(\frac{\text { me kB T1 }}{2 \pi \hbar^{2}}\right)^{3 / 2} / /$. rule1
$1.25471 \times 10^{19}$
$n 1=n Q \operatorname{Exp}\left[-\frac{\beta \Delta}{2}\right] / /$. rule1
$5.69637 \times 10^{14}$

## 7. Electron positron pair (R. Baierlein, Thermal Physics (Cambridge, 2001).

 In the extremely hot interior of stars, gamma rays can form an electron-positron pair,$$
e^{+}+e^{-} \Leftrightarrow \gamma+\gamma
$$

and the pair can mutually annihilate to form two gamma rays. Moreover, this process occurred in the early evolution of our universe. In thermal equilibrium, we have

$$
\mu_{e^{+}}+\mu_{e^{-}}=0
$$

since the chemical potential of photon is zero. Then we have

$$
\left[e^{+}\right]\left[e^{-}\right]=4 n_{e+} n_{e-} \exp \left(-2 \beta m c^{2}\right)=4\left(\frac{2 \pi m k_{B} T}{h^{3}}\right)^{3} \exp \left(-2 \beta m c^{2}\right)
$$

where $m c^{2}$ is the rest energy of the electron and positron and the factor 4 comes from the spin factor $(2 S+1)=2$ for electron and positron (both spin $1 / 2$ ).

The core of a hot, massive star (of mass equal to 12 solar masses, say) may have a temperature of $T=10^{9} \mathrm{~K}$. The right side has the value $1.64877 \times 10^{53} \mathrm{~cm}^{-6}$, a reasonable value for such a star. If $\left[e^{-}\right]=3 \times 10^{27} \mathrm{~cm}^{-3}$, we have $\left[e^{+}\right]=5.4959 \times 10^{25} \mathrm{~cm}^{-3}$. That is, there is one positron for every $54.586 \approx 55$ electrons.
If $\left[e^{+}\right]=\left[e^{-}\right]$, we have

$$
\left[e^{+}\right]=\left[e^{-}\right]=4.06 \times 10^{26} \mathrm{~cm}^{-3} .
$$

## ((Mathematica))

## Clear["Global`*"];

$$
\begin{aligned}
& \text { rule1 }=\left\{\mathrm{kB} \rightarrow 1.3806504 \times 10^{-16}, N A \rightarrow 6.02214179 \times 10^{23},\right. \\
& \mathrm{c} \rightarrow \rightarrow 2.99792 \times 10^{10}, \mathrm{~h} \rightarrow 2 \pi \hbar, \hbar \rightarrow 1.05457162810^{-27}, \\
& \mathrm{me} \rightarrow 9.1093821510^{-28}, \mathrm{mp} \rightarrow 1.672621637 \times 10^{-24}, \\
& \mathrm{mn} \rightarrow 1.674927211 \times 10^{-24}, \mathrm{qe} \rightarrow 4.8032068 \times 10^{-10}, \\
& \mathrm{eV}\left.\rightarrow 1.602176487 \times 10^{-12}\right\} ; \\
& \mathrm{nQ}=\left(\frac{2 \pi \mathrm{me} \mathrm{kB} \mathrm{~T}}{\mathrm{~h}^{2}}\right)^{3 / 2} / / \text { rule1 } \\
& 2.41469 \times 10^{15} \mathrm{~T}^{3 / 2}
\end{aligned}
$$

$\mathrm{f}\left[\mathrm{T} 1_{-}\right]:=4 \mathrm{nQ}^{2} \operatorname{Exp}\left[\frac{-2 \mathrm{me} \mathrm{c}^{2}}{\mathrm{kB} \mathrm{T}}\right] / . \mathrm{T} \rightarrow \mathrm{T} 1 / /$. rule1
$\mathrm{k} 1=\mathrm{f} 1\left[10^{9}\right]$
$1.64877 \times 10^{53}$
$\mathrm{g} 1=3 \times 10^{27} ; \mathrm{g} 2=\mathrm{k} 1 / \mathrm{g} 1$
$5.49591 \times 10^{25}$
g1/g2
54.586
((Note))
At extremely high temperatures, comparable with the rest energy $m c^{2}$ of the electron, collisions of particles in matter may be accompanied by the formation of electron-positron pairs. The number of particles itself then causes to be a given quantity, and depends on the conditions of thermal equilibrium. Pair production (and the reverse process, annihilation) can be regarded thermodynamically as a chemical reaction

$$
e^{+}+e^{-}=\gamma
$$

where the symbols $e^{+}$and $e^{-}$denote a positron and an electron, and $\gamma$ denotes one or more photons. The chemical potential of the photon gas is zero. The condition of equilibrium for pair production is therefore

$$
\mu^{+}+\mu^{-}=0
$$

where $\mu^{-}$and $\mu^{+}$are the chemical potentials of the electron and positron gases. It should be noted that m here denotes the relativistic expression for the chemical potential, including the rest energy of the particles, which plays an important part in pair production.

## REFERENCES

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980). R. Baierlein, Thermal Physics (Cambridge, 2001).
L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon Press 1976).

## APPENDIX

## Saha equation (Fermi)

In Na vapor at very high temperatures, Na atoms become ionized. They lose one of their electrons, and thus changed into ions.

$$
\mathrm{Na}(\text { atom }) \Leftrightarrow \mathrm{Na}^{+}(\text {ion })+e^{-}(\text {electron }) .
$$

It is found that, at any given temperature, this ionization reaction reaches a state of thermal equilibrium which is quite analogous to the chemical equilibrium for ordinary chemical reactions.

$$
\begin{aligned}
\frac{[\mathrm{Na}]}{\left[\mathrm{Na}^{+}\right]\left[e^{-}\right]} & =\frac{n_{Q}(\mathrm{Na})}{n_{Q}\left(\mathrm{Na}^{+}\right) n_{Q}\left(e^{-}\right)} \exp \left\{-\beta\left[E(\mathrm{Na})-E\left(\mathrm{Na}^{+}\right)-E\left(e^{-}\right)\right]\right. \\
& =\frac{h^{3}}{(2 \pi m)^{3 / 2}} \beta^{3 / 2} \exp (\beta \Delta E)
\end{aligned}
$$

where we use

$$
n_{Q}\left(\mathrm{Na}^{+}\right)=n_{Q}(\mathrm{Na})
$$

Let $x$ be the degree of ionization, that is, the fraction of atoms that are ionized;

$$
x=\frac{\left[\mathrm{Na}^{+}\right]}{\left[\mathrm{Na}^{+}\right]+[\mathrm{Na}]}
$$

and let $n=\left[\mathrm{Na}^{+}\right]+[\mathrm{Na}]$ be the total concentration of the sodium (atoms and ions). Then we have

$$
\left[\mathrm{Na}^{+}\right]=n x, \quad[\mathrm{Na}]=n(1-x)
$$

Since there is obviously one electron present for each sodium ion, we have

$$
\left[\mathrm{e}^{-}\right]=\left[\mathrm{Na}^{+}\right]=n x
$$

and we finally obtain

$$
\frac{1}{n}\left(\frac{1-x}{x^{2}}\right)=\frac{h^{3}}{(2 \pi m)^{3 / 2}} \beta^{3 / 2} \exp (\beta \Delta E)
$$

or

$$
\begin{aligned}
n\left(\frac{x^{2}}{1-x}\right) & =\frac{\left(2 \pi m k_{B}\right)^{3 / 2}}{h^{3}} T^{3 / 2} \exp \left(-\frac{\Delta E}{k_{B} T}\right) \\
& =2.41469 \times 10^{15} T^{3 / 2} \exp \left(-\frac{\Delta E}{k_{B} T}\right)
\end{aligned}
$$

(Saha equation)
where $n$ is the total concentration of the sodium (atoms and ions).
((Note)) Saha equation
The Saha ionization equation, also known as the Saha-Langmuir equation, is an expression that relates the ionization state of a gas in thermal equilibrium to the temperature and pressure. The equation is a result of combining ideas of quantum mechanics and statistical mechanics and is used to explain the spectral classification of stars. The expression was developed by the Indian astrophysicist Meghnad Saha in 1920, and later (1923) by Irving Langmuir.
https://en.wikipedia.org/wiki/Saha_ionization_equation

