Diffusion

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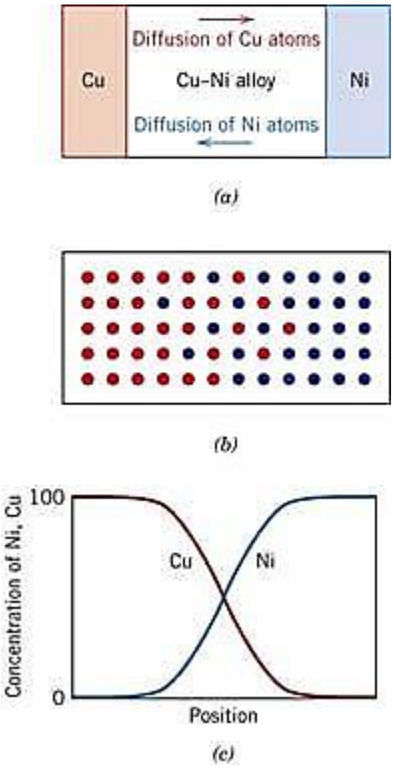
The atoms in a crystal in addition to vibrating to their mean position, can also change their position by moving into adjoining vacant sites, a process known as diffusion. Diffusion can be defined as the mechanism by which matter is transported through matter. The diffusion process is defined as a net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion. Basically, in is the movement of molecules from an area of higher concentration to a lower area. Atoms in gases, liquids and solids are in constant motion and migrate over a period of time. In gases the atomic movement is relatively rapid. Atomic movements in liquids are in general slower than in gases. In solids, the atomic movements are restricted due to bonding to equilibrium positions. However, thermal vibration occurring in solids do allow some atoms to move.



(a)

(b)

(c)

Diffusion of atoms in metals and alloys is particularly important since most solid state reactions involve atomic movements.

The following factors affects the diffusion process:

i) Concentration
ii) vibrational frequency
iii) Temperature
iv) Bond energy
v) Activation energy
vi) Crystal structure
vii) Energy barriers of atomic motion
viii) Bonding of atoms to equilibrium position

Atomic mechanisms of diffusion/ physical process of diffusion:

For diffusion process there are following four main mechanisms in a crystalline lattice, such as

i) Vacancy or substitutional diffusion mechanism
ii) Interstitial diffusion mechanism
iii) Interstitialcy diffusion mechanism
iv) Ring or exchange mechanism

Vacancy or substitutional mechanism

Vacancy diffusion occurs in crystal lattice by movement of atoms from one atomic site to another if there is sufficient activation energy present provided by the thermal vibration of the atoms and if there are vacancies of other crystal defects in the lattice for atoms to move into neighboring atoms ant thereby fill up the vacancy. After one such movement the new vacancy can receive another atom and the process is continued and that is migration of vacancy also takes place with the migration of an atom in a vacancy.

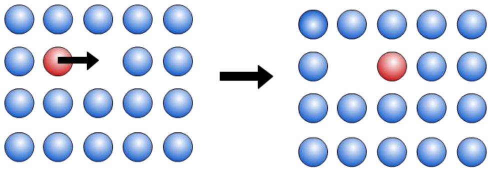


Fig. 1: Vacancy or substitutional diffusion

Interstitial diffusion mechanism

The interstitial diffusion of atoms in crystal lattices takes place when atoms moves from one interstitial site to another neighboring interstitial site without permanently displacing any of the atoms in the matrix crystal lattice, i.e. diffusion of interstitial atom to interstitial place.

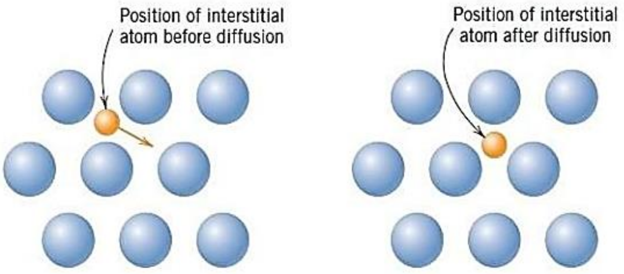


Fig. 2: Interstitial diffusion

Interstitialcy Diffusion Mechanism

The interstitialcy diffusion mechanism in crystal lattices takes place when migration of atom from lattice point to interstitial point as shown in fig.3

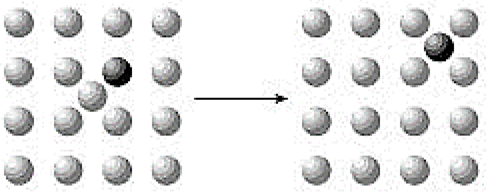


Fig.3: Interstitialcy Diffusion

Ring or Exchange Mechanism

In exchange mechanism two atom of lattice point interchange their position. In ring mechanism more than two atoms of lattice point interchange their position in such a pattern that it seems like a ring.

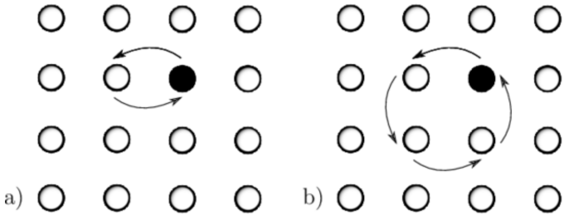


Fig.4: Ring or Exchange

Characteristics of Solid State Diffusion Process:

i) Diffusion is net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion.
ii) In solid, the atomic movement are restricted due to bonding to equilibrium position. However thermal vibration occurring in solid do allow some atoms to move.
iii) Inhomogeneous materials can become homogeneous by diffusion.
iv) For an active diffusion to occurs, the temperature should be high enough to overcome energy barriers of atomic motion.
v) Interstitial diffusion depends on temperature. This is generally faster than vacancy diffusion because there are many interstitial sites than vacancy site to jump to.
vi) Interstitial diffusion occurs in response to a concentration gradient.
vii) Vacancy diffusion occurs in crystal lattices by the movement of atoms from one atomic site to another if there sufficient activation energy present provided by the thermal vibration of atoms and if there are vacancies or other crystal defects in the lattice.
viii) In non-steady state diffusion, the concentration gradient are changing with time.
ix) In self-diffusion the atoms that exchange positions are of the same type.

Fick's law of Diffusion:

In 1855, physiologist Adolf Fick first reported his well-known laws governing the transport of mass through diffusive means. Fick's work was inspired by the earlier experiments of Thomas Graham, which fell short of proposing the fundamental laws for which Fick would become famous. The Fick's law is analogous to the relationships discovered at the same epoch by other eminent scientists: Darcy's law (hydraulic flow), Ohm's law (charge transport), and Fourier's Law (heat transport).

Fick's First Law

Fick's first law relates the diffusive flux to the concentration under the assumption of **steady state**. **It postulates that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative)**, or in simplistic terms the concept that a solute will move from a region of high concentration to a region of low concentration across a concentration gradient. In one (spatial) dimension, the law can be written in various forms, where the most common form is in a molar basis:

$$J \propto -\frac{dC}{dx}$$

$$J = -D\frac{dC}{dx}$$

Where

- J is the **diffusion flux**, of which the dimension is amount of substance per unit area per unit time, so it is expressed in such units as mol m^{-2} s^{-1}. J measures the amount of substance that will flow through a unit area during a unit time interval.
- D is the **diffusion coefficient** or **diffusivity**. Its dimension is area per unit time, so typical units for expressing it would be m^2/s.
- C (for ideal mixtures) is the concentration, of which the dimension is amount of substance per unit volume. It might be expressed in units of mol/m^3.
- x is position, the dimension of which is length. It might thus be expressed in the unit m.

The negative sign indicates that J is positive when movement is down the gradient, i.e., the negative sign cancels the negative gradient along the direction of positive flux.

D is proportional to the squared velocity of the diffusing particles ($D \propto V^2$), which depends on the temperature, viscosity of the fluid and the size of the particles according to the Stokes–Einstein relation. In dilute aqueous solutions the diffusion coefficients of most ions are similar and have values that at room temperature are in the range of $(0.6–2) \times 10^{-9}$ m^2/s. For biological molecules the diffusion coefficients normally range from 10^{-11} to 10^{-10} m^2/s.

In two or more dimensions we must use ∇, the del or gradient operator, which generalizes the first derivative, obtaining

$$\boldsymbol{J} = -D\boldsymbol{\nabla}C$$

Where **J** denotes the diffusion flux vector.

The driving force for the one-dimensional diffusion is the quantity $-\partial C/\partial x$, which for ideal mixtures is the concentration gradient.

Fick's second law

Fick's second law predicts how diffusion causes the concentration to change with time (non-steady state). If C is not constant at any one point and variation of C with time is required, this can be expressed by Fick’s 2nd law as:

$$\frac{dC}{dt} = \frac{d}{dx}\left(D\frac{dC}{dx}\right)$$

$$= D\frac{d^2C}{dx^2}$$

Where

- C is the concentration in dimensions of [(amount of substance) length^{-3}], example mol/m^3; C=C(x,t) is a function that depends on location x and time t
- t is time, example s
- D is the diffusion coefficient in dimensions of [length^2 time^{-1}], example m^2/s
- x is the position [length], example m

In two or more dimensions we must use the Laplacian $\Delta = \nabla^2$, which generalizes the second derivative, obtaining the equation

$$\frac{dC}{dt} = D\nabla^2 C$$

$$\frac{dC}{dt} = D\Delta C$$

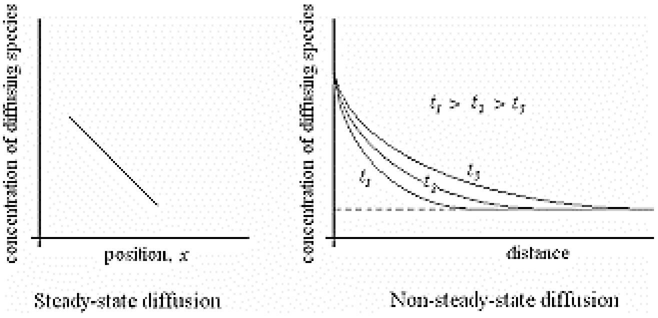


Fig. 5: Steady and non-steady state of diffusion

Thermally Activated Process

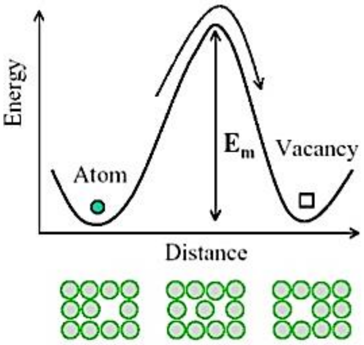


Fig. 6: Schematic representation of the diffusion of an atom from its original position into a vacant lattice site

Many physical and chemical processes strongly depend on temperature and exhibit what is called an Arrhenius type behavior, in which the rate of change is proportional to exp(– EA/kT), where EA is a characteristic energy parameter applicable to the particular process. Processes that exhibit an Arrhenius type temperature dependence are referred to as thermally activated.

The average thermal energy of an atom (K_BT= 0.026 eV at room temperature) is usually much smaller than E_m = (~1eV/atom) and a large fluctuation in energy is needed for a jump. The probability of such fluctuation of frequency of jump R_j, Depends exponentially on temperature is given as

$$\mathrm{Rj} = R_0 e^{\left(\frac{-E_m}{K_B T}\right)} \qquad \text{(Arrhenius Equation)}$$

R_0 is called attempt frequency. Which is proportional to the frequency of atomic vibration. If there are no vacant sites, then no jump.

The probability of finding a vacant site in an adjacent lattice

$$\mathrm{P} = \mathrm{Z} e^{\left(\frac{-Q_v}{K_B T}\right)}$$

Where Z is the coordination number (the number of atoms or ions immediately surrounding a central atom in a complex or crystal) and Q_v is the activation energy for vacant site

The diffusion coefficient is proportional to the probability of finding a vacant site and the frequency of jump. Then it can be written as $D = R_jPa^2$

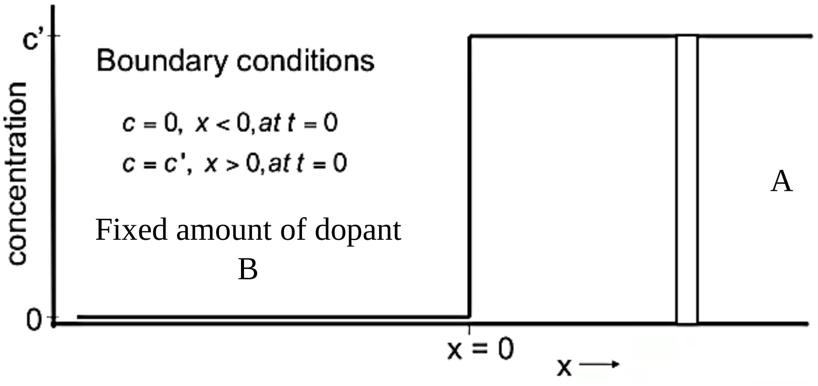
$$D \approx Z R_0 a^2 e^{\left(\frac{-Q_v - E_m}{K_B T}\right)}$$

$$D = D_0 e^{\left(\frac{-Q_d}{K_B T}\right)}$$

Where $D_0 = Z R_0 a^2$ and $Q_d = Q_v + E_m$

Solution of Fick’s 2nd Law

(Doping of steel with carbon or doping with fixed amount of dopant:)



Let us consider this layer of fixed amount of dopant B diffusing into A, through annealing at high temperature. From Fick’s second law we know

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad (1)$$

The solution of this equation is

$$C(x,t) = \frac{\beta}{\sqrt{t}}e^{-\frac{x^2}{4Dt}} \qquad (2)$$

Where C(x,t) is the concentration of the diffusing atoms at any position at any time. β is a constant determined by the boundary conditions, this is also concentration at boundary.

$$\int_0^{\propto} C(x,t)dx = \int_0^{\propto} \frac{\beta}{\sqrt{t}}e^{-\frac{x^2}{4Dt}}\,dx = N = constant \qquad (3)$$

$$\int_0^{\propto} C(x,t)dx = constant \qquad (4)$$

Let, $y = \frac{x}{2\sqrt{Dt}}$

so that, $dy = \frac{dx}{2\sqrt{Dt}}$

or, $dx = 2\sqrt{Dt}\,dy$

putting this value in equation 3 we get

$$\int_0^{\propto} \frac{\beta}{\sqrt{t}}e^{-y^2}2\sqrt{Dt}\;dy = N$$

$$\frac{\beta}{\sqrt{t}}2\sqrt{Dt}\;\int_0^{\propto} e^{-y^2}dy = N \qquad \left[\int_0^{\propto} e^{-y^2}dy = \frac{\sqrt{\pi}}{2}\right]$$

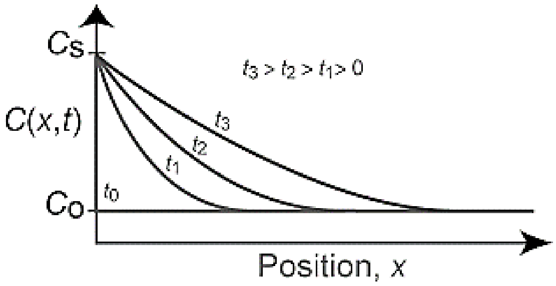
$$\beta = \frac{N}{\sqrt{\pi D}}$$

(4)

So,

$$C(x,t) = \frac{N}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

This equation describe the diffusion kinetics or profile of diffusing concentration.



In the above we considered one dimensional one way diffusion ($0 \; to \propto$) only, but if we extends it into two way for ($-\propto \; to {+}\propto$) with dopant at x=0, thus we have

$$\beta = \frac{N}{2\sqrt{\pi D}}$$

Then,

$$C(x,t) = \frac{N}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

Fick's 1st law in interstitial diffusion

In the case of interstitial diffusion, the movement of an atom from one interstitial site to another (e.g. carbon in ($\propto -iron$) or the migrating atom has to overcome a potential barrier at the time of passing over. If the barrier is of height E, the atoms will have sufficient thermal energy to pass over the barrier only a fraction $e^{\left(\frac{-E}{K_BT}\right)}$ of time.

At a given temperature, T, if R_0 is the characteristic frequency or the attempt frequency of the atom, then the probability R_J that sometime during the atom will have enough thermal energy to pass over the barrier is

$$R_J = R_0 e^{\left(\frac{-E}{K_BT}\right)} \tag{1}$$

Where R_J is also known as the jump frequency and its value is of the order of 10^{14} Hz.

Now, the diffusivity, D is often found to vary with temperature as

$$D = D_0 e^{\left(\frac{-E}{K_BT}\right)} \tag{2}$$

To find the temperature dependency of D, we consider two parallel planes of the impurity atoms in the interstitial sites. The planes are separated by lattice constant ‘a’. There are S (atoms/cm^2) impurity atoms in one plane and (S + a$\frac{dS}{dx}$) (atoms/cm^2) on the other.

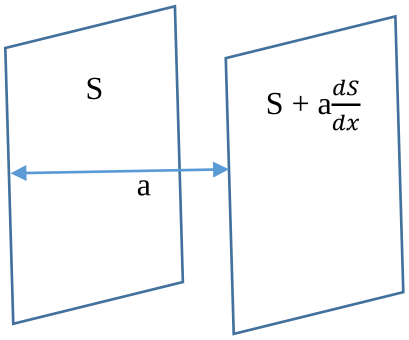


Fig. 1

The net number of atoms crossing between the planes in one second is

$$J_N \approx -R_J a \frac{dS}{dx} \tag{3}$$

If N is the total concentration of impurity atoms, then S=aN per cm^2 of a plane. The flux may now be written as

$$J_N = -R_J a \frac{d}{dx}(aN)$$

$$= -R_J a^2 \frac{dN}{dx} \tag{4}$$

Putting the value of R_J in this eqn we get

$$J_N = -R_0 e^{\left(\frac{-E}{K_B T}\right)} a^2 \frac{dN}{dx} \tag{5}$$

From Fick’s 1st law, the no. of atoms crossing unit area in unit time is

$$J_N = -D \frac{dN}{dx} \tag{6}$$

Comparing eqn(5) and eqn(6) we obtain,

$$D = -R_0 a^2 e^{\left(\frac{-E}{K_B T}\right)} \tag{7}$$

Which describe th mechanism of carbon diffusion in $\propto -iron$ in isothermal condition.

Now from eqn 2 and 6 we have

$$D_0 = -R_0 a^2$$

The Gibbs Free Energy *or Gibbs energy or Gibbs function or simply the free enthalpy is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric). The Gibbs free energy ($\Delta G^o = \Delta H^o - T\Delta S^o$; J in SI units) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system.*

The Helmholtz Free Energy *is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume (isothermal, isochoric).*

Chemical Potential *of a species is energy that can be absorbed or released due to a change of the particle number of the given species, e.g. in a chemical reaction or phase transition. The chemical potential of a species in a mixture is defined as the rate of change of a free energy of a thermodynamic system with respect to the change in the number of atoms or molecules of the species that are added to the system. Thus, it is the partial derivative of the free energy with respect to the amount of the species, all other species' concentrations in the mixture remaining constant. The molar chemical potential is also known as partial molar free energy. When both temperature and pressure are held constant, chemical potential is the partial molar Gibbs free energy. At chemical equilibrium or in phase equilibrium the total sum of the product of chemical potentials and stoichiometric coefficients is zero, as the free energy is at a minimum.*

In semiconductor physics, the chemical potential of a system of electrons at a temperature of zero Kelvin is known as the Fermi energy.

Hydrogen Diffusion (Permeation of hydrogen)

Diffusion with saturable traps The diffusion of hydrogen in metals is of great interest because some alloys can store large amounts of hydrogen while others become brittle by it (e.g. ∝-iron). Hydrogen, as a very small atom, is highly mobile between the interstices of metals so that diffusion can be measured near room temperature. There is even the possibility of quantum mechanical tunneling of hydrogen in the bcc lattice. There are many experimental methods available to measure hydrogen diffusion, e.g. gas pressure, electromotive force (e.m.f.), dilatometry (*a thermo-analytical method for measuring the shrinkage or expansion of materials over a controlled temperature regime*), electrical resistance, magnetic susceptibility, neutron scattering etc. In this section we concentrate on the influence of the microstructure on hydrogen diffusion: lattice defects provide saturable 'traps' for hydrogen where it forms bound states so that it is no longer available for diffusion and solution. Palladium dissolves large amounts of hydrogen at moderate temperatures and pressures, measured by the ratio: $n = C_H/C_{Pd}$.

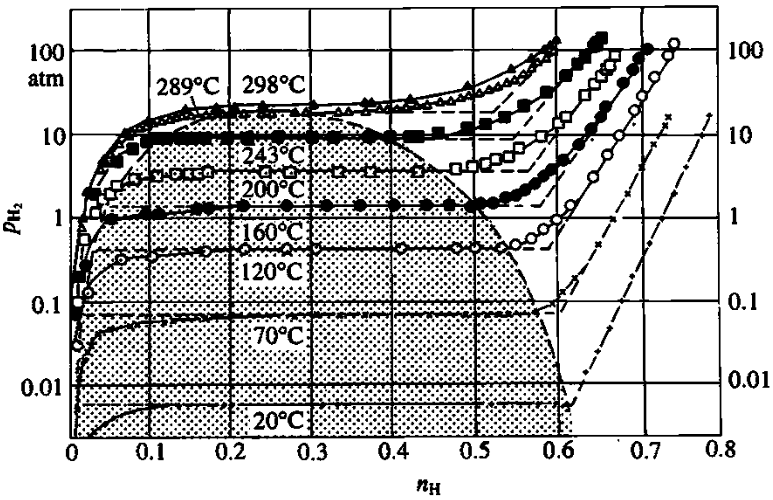


Fig.1: Phase diagrams (P, n, T) of Pd-H with (shaded) two phase region $(\alpha + \beta)$

Thermodynamics and diffusion in nearly perfect Pd—H

Diffusin takes plase due to change in chemical potential μ. Chemical potential μ depends on several parameters of the system and is measured by several thermochemical methods. One method is the measurement of partial free energy of mixing. It is the work done on reversibly adding one mole of the pure substance (H) to a large amount of the alloy (Pd-H), by isothermal distillation for which

$$\mu = \frac{\partial G^m}{\partial n_H} = RTln\frac{P_H}{P_{Pd-H}} \tag{1}$$

Where G^m is the Gibb's free energy of the mixing.

The term in the left hand side of (1) is the partial energy of mixing and is the chemical potential. P_H is the partial pressure of hydrogen over the alloy and P_{Pd-H} is the partial pressure of pure Pd-component. $\frac{P_H}{P_{Pd-H}}$ is known as the activity of the solution, a_H.

Therefore,

$$\mu = \frac{\partial G^m}{\partial n_H} = RTlna_H \tag{2}$$

The partial energy of mixing $\frac{\partial G^m}{\partial n_H}$ can also be measured by electrolytic transfer in a galvanic double cell with Pd membrane.

In the present case, the chemical potential of the system as a whole is

$$\mu = \mu_H^o + RTln\frac{P_H}{P_{Pd-H}} \tag{3}$$

$$= \mu_H^o + RTln\frac{\frac{C_H}{C_{Pd}}}{1-\frac{C_H}{C_{Pd}}}$$

Where C’s are concentrations.

Since the alloy is in equilibrium with the hydrogen gas (H_2 molecules), the chemical potential of hydrogen atom in the alloy can be written as

$$\frac{1}{2}\mu_{H_2} = \mu_H = \frac{1}{2}\mu_{H_2}^o + \frac{1}{2}RTln\frac{n_H}{1-n_H}$$

$$\mu_H = \frac{1}{2}\mu_{H_2}^o + \frac{1}{2}RTlnP_{H_2}$$

$$= \frac{1}{2}\mu_{H_2}^o + RTln\sqrt{P_{H_2}} \qquad (4)$$

Eqn(4) shows that the activity a_H of hydrogen is given by $\sqrt{P_{H_2}}$ in such a system as evident from eqn(2). Hence, from eqn(4) we get

$$a_H = e^{\left(\frac{\mu_H-\frac{1}{2}\mu_{H_2}^o}{RT}\right)}$$