STATISTICAL MECHANICS

Consider an ideal monatomic gas.

The particles are indistinguishable, but it is possible in principle to determine which (translational) energy levels are occupied.

Consider a system of three particles (1, 2, 3) occupying three states a, b, c.

Total eigenfunction (un normalised) is given by

$$
\begin{aligned}
\Psi = \ & \psi_a\ (1)\ \psi_b\ (2)\ \psi_c\ (3) \\
& \mp \psi_a\ (2)\ \psi_b\ (1)\ \psi_c\ (3) \\
& + \psi_a\ (2)\ \psi_b\ (3)\ \psi_c\ (1) \\
& \mp \psi_a\ (3)\ \psi_b\ (2)\ \psi_c\ (1) \\
& + \psi_a\ (3)\ \psi_b\ (1)\ \psi_c\ (2) \\
& \mp \psi_a\ (1)\ \psi_b\ (3)\ \psi_c\ (2)
\end{aligned}
$$

Upper sign wavefunction is antisymmetric with respect to interchange of particles - corresponds to Fermi-Dirac statistics which apply to electrons, protons, neutrons and species containing an odd total number of these particles (e.g. deuterium atom).

Lower sign wavefunction is symmetric - Bose-Einstein statistics which apply to H, He etc. which contain an even number of p, n, e. Note:- Fermi-Dirac statistics give Pauli exclusion principle since no two ψ can be identical. Bose-Einstein statistics give no such restriction.

For 3 particles we would have $3! = 6$, arrangements in above example if particles were distinguishable. Quantum statistics give only one wavefunction

Fermi-Dirac Statistics [*]

Assume we can group the energy levels. Let there be N_i particles in the g_i levels of energy ε_i . $g_i \gg N_i$ from the exclusion principle.

Since we can tell in principle which levels are occupied number of distinguishable arrangements (w_i) is

$$
w_i = \frac{g_i!}{N_i!\,(g_i - N_i)!}
$$

For whole system total number of possible configurations is

$$
W = \prod_i w_i = \prod_i \left\{ \frac{g_i!}{N_i!\,(g_i - N_i)!} \right\}
$$

[*] Note use of Fermi-Dirac form in this handout ; see top of p2

At 'high' temperatures ($g_i \gg N_i$) Fermi-Dirac (and Bose-Einstein) statistics become equivalent to Boltzmann

$$W = \prod_i \left(\frac{g_i\,N_i}{N_i!} \right)$$

Constraints for equilibrium in a closed system

a) Conservation of particles $\qquad N = \sum_i N_i$

$\qquad dN = \sum dN_i = 0$

b) Conservation of energy $\qquad E = \sum_i N_i \varepsilon_i$

$\qquad dE = \sum_i \varepsilon_i\, dN_i = 0$

c) Constant volume $\qquad [\varepsilon = \frac{n^2 h^2}{8mL^2}$ for 1-D translation]

$\qquad \varepsilon_i = 0$ for translation.

d) W is a maximum - i.e. system has most probable distribution

Stirling's approximation $\ln x! = x \ln x - x$.

$$\ln W = \sum_i [g_i \ln g_i - g_i - N_i \ln N_i + N_i - (g_i - N_i)$$
$$\ln (g_i - N_i) + g_i - N_i]$$
$$= \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln(g_i - N_i)]$$
$$\simeq \sum_i N_i \ln (g_i/N_i) \qquad \text{if } g_i \gg N_i \qquad \text{``}\neq\text{``}$$

$$d(\ln W) = \sum_i [-1 - \ln N_i + 1 + \ln (g_i - N_i)]\, dN_i$$
$$= \sum \ln [(g_i - N_i)/N_i]\, dN_i.$$
$$= 0, \quad \text{to maximise}$$

Combining with (a) and (b) from above

$$\sum_i [\ln \frac{(g_i - N_i)}{N_i} - \alpha - \beta \varepsilon_i]\, dN_i = 0 \qquad \left(Lagrange \right)$$

Each term in brackets must be zero, since relation must hold for any N_i

$$\frac{g_i - N_i}{N} = e^{\alpha} e^{\beta \varepsilon_i}$$

Corresponding treatment for Bose-Einstein statistics gives:

$$\frac{g_i + N_i}{N_i} = e^{\alpha} e^{\beta \varepsilon_i}$$

Normally $\varepsilon_i \ggg N_i$

Hence $\dfrac{N_i}{g_i} = e^{-\alpha} e^{-\beta \mathcal{E}_i}$

Possible exceptions   a)   very high pressures

b)   very low temperatures

c)   electrons (very low mass)

$$N = \sum_i N_i = e^{-\alpha} \sum_i g_i e^{-\beta \mathcal{E}_i}$$

$$\frac{N_i}{N} = \frac{g_i e^{-\beta \mathcal{E}_i}}{\sum_i g_i e^{-\beta \mathcal{E}_i}} \qquad \frac{E}{N} = \frac{\sum_i g_i \mathcal{E}_i e^{-\beta \mathcal{E}_i}}{\sum_i g_i e^{-\beta \mathcal{E}_i}}$$

↰ DISTRIBUTION LAW

Equipartition

Simple case without degeneracy:

$$n_i = \frac{N e^{-\beta \mathcal{E}_i}}{\sum e^{-\beta \mathcal{E}_i}}$$

Let us take $\mathcal{E}_i$ increments to be defined in terms of __momentum__ increase.

i.e. states are $f(p)$, $f(p + \triangle p)$ ... etc.

$$\therefore \quad i = \frac{N e^{-\beta f_i(p)}}{\sum e^{-\beta f_i(p)}}$$

Multiply top & bottom by $\triangle p$

$$n_i = \frac{N e^{-\beta f(p)}}{\sum -\beta f(p)} \frac{\triangle p}{\triangle p}$$

If now we consider $\underset{\triangle p \to 0}{Lt}$, n_i is replaced by $\emptyset (p) dp$

[a continuous distrib^n]

$$\emptyset(p) dp = \frac{N e^{-\beta \mathcal{E}} dp}{\int e^{-\beta \mathcal{E}} dp}$$

$$\int e^{-\beta \mathcal{E}} dp = [p e^{-\beta \mathcal{E}}]_{p=0}^{\infty} + \beta \int p e^{-\beta t} \frac{dt}{dp} \cdot dp$$

$$\underbrace{\qquad}_{\quad \to \;\; = 0}$$

Hence $\dfrac{1}{\beta} = \dfrac{\int p \frac{d\mathcal{E}}{dp} e^{-\beta \mathcal{E}} dp}{\int e^{-\beta \mathcal{E}} dp} = \dfrac{\int \phi(p) \left[p \frac{d\mathcal{E}}{dp} \right] dp}{N}$

and this is the AVERAGE value of $p \frac{d\mathcal{E}}{dp}$ so that

$$\frac{1}{\beta} = \overline{\left(p \frac{d\mathcal{E}}{dp} \right)} \; ;$$ and is the same for all momentum coordinates

If energy is a square term

$$\varepsilon = ap^2$$

$$\frac{d\varepsilon}{dp} = 2ap$$

$$\therefore \; p\frac{d\varepsilon}{dp} = 2ap^2 = 2\varepsilon$$

Thus FOR ALL SQUARE TERMS

$$2\bar{\varepsilon} = 1/\beta$$

$$\text{or} \quad \bar{\varepsilon} = 1/2\beta$$

Identity of β

One approach DEFINES k (Boltzmann constant) via

$$\beta = 1/kT \qquad (\text{i.e. } \bar{\varepsilon} = \tfrac{1}{2}kT)$$

Now the gas law gives $PV = \tfrac{1}{3}Nm\bar{c}^2 = RT$

$$\therefore \quad \tfrac{1}{3}m(\bar{\dot{x}}^2 + \bar{\dot{y}}^2 + \bar{\dot{z}}^2) = \frac{RT}{N}$$

$$\bar{\dot{x}}^2 = \bar{\dot{y}}^2 = \bar{\dot{z}}^2 \qquad \therefore \quad m\bar{\dot{x}}^2 = \frac{RT}{N}$$

$$\therefore \; \bar{\varepsilon} = \tfrac{1}{2}\frac{RT}{N} \implies \frac{RT}{N} = kT \;\therefore\; k = R/N$$

Relation between Entropy and Disorder

Suppose there exists a relation, $S = f(W)$

Entropy is additive, disorder (probability) is multiplicative

i.e. $S_1 + S_2 = f(W_1 \times W_2)$

Therefore the function is logarithmic: $S = \lambda \ln W$

$$\therefore \; \delta S = \lambda \cdot \delta \ln W = -\lambda \sum \ln \frac{n_i}{g_i} \delta n_i$$

$$\therefore \; dS = -\lambda \sum_i \ln \frac{n_i}{g_i} \, dn_i = -\lambda \sum (\alpha - \beta \varepsilon_i) \, dn_i$$

$$= \lambda \alpha \, dN + \lambda \beta \, dE$$

But $dE = T dS \; (\overbrace{\cdots PdV}) + \mu \, dN$

(constant V)

or $dS = \frac{1}{T} dE - \frac{\mu}{T} dN$ $\left.\right\} \Rightarrow$

$\lambda \beta = \frac{1}{T} = \frac{\lambda}{kT}$

$\lambda = k$

$\lambda \alpha = k\alpha = -\mu / T$

$\alpha = -\mu / kT$

THUS: I $\quad S = k \ln W$

II $\quad \dfrac{n_i}{g_i} = e^{(\mu - \varepsilon_i)/kT}$

Partition functions

$$n_i = g_i \, e^{(\mu - \varepsilon_i)/kT}$$
$$\therefore \; N = \sum_i n_i = e^{\mu/kT} \sum_i g_i \, e^{-\varepsilon_i/kT}$$

Note that $\sum_i g_i \, e^{-\varepsilon_i/kT} = \sum e^{-\varepsilon/kT}$

(summed over "bunches")   (summed over individual levels)

We define $f = \sum_i g_i \, e^{-\varepsilon_i/kT}$,   the <u>partition function</u>

which is a function of the available levels and the temperature

i.e. $N = e^{\mu/kT} f$

or $\mu = kT \ln (N/f)$

We can now use the definition of f to yield expressions for $E \; (\equiv U)$, S, A etc.

We note that $\left(\dfrac{df}{dT} \right)_V = \sum g_i \dfrac{\varepsilon}{kT^2} e^{-\varepsilon_i/kT}$

INTERNAL ENERGY E $(\equiv U)$

$$E = \sum_i N_i \varepsilon_i \qquad = \frac{N}{f} \sum_i \varepsilon_i g_i \, e^{-\frac{\varepsilon_i}{kT}}$$

$$E = \frac{NkT^2}{f}\frac{df}{dT} = NkT^2\left(\frac{d\ln f}{dT}\right)$$

ENTROPY S

Put $S = k \ln W$, and take expression "$\ddagger$" for $(\ln W)$ on p2

$$S = k\sum N_i \ln(g_i/N_i) = -k\sum N_i\left[\ln\frac{N}{f} - \frac{\varepsilon_i}{kT}\right]$$

$$= -Nk\ln\frac{N}{f} + \frac{E}{T}$$

$$\therefore \; S = Nk\left\{T\frac{d\ln f}{dT} - \ln\frac{N}{f}\right\}$$

HELMHOLTZ FREE ENERGY

$$A = E - TS.$$

$$= -NkT\ln\frac{f}{N}$$

$$P = -\left\{\frac{\partial A}{\partial V}\right\}_T \qquad = \quad NkT\left\{\frac{d\ln f}{dv}\right\}_T$$

$$H = E + PV \qquad\qquad G = A + PV.$$

Note that the expressions for S, A etc depend on the inequality $g_i \gg N_i$. Derivations leaving this approximation till later give slightly different results

PARTITION FUNCTIONS FOR TRANSLATION

Monatomic gas in one dimension.

$$\varepsilon_x = \frac{N_x^2 h^2}{8m L^2}$$

$$f_x = \sum_{n_x = 1}^{n_x = \infty} \exp\left(-\frac{n^2 h^2}{8m L^2 kT.}\right) \;\simeq\; \int_0^\infty \exp(- \quad)\, dn_x$$

$$\int_0^\infty e^{-ax^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{a.}}$$

$$f_x = \frac{(2\pi m\, k\, T)^{\frac{1}{2}}}{h} l$$

Translation in three dimensions

Each motion independent

$$\varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z$$

Every term in f_{tr} corresponds to every term in $f_x\, f_y\, f_z$ since

$$e^{-\frac{\varepsilon}{kT}} = e^{-\frac{\varepsilon_x}{kT}}\; e^{-\frac{\varepsilon_y}{kT}}\; e^{-\frac{\varepsilon_z}{kT}}.$$

$$\therefore \quad f_{1n} = f_x \, f_y \, f_z$$

$$= \frac{(2\pi mkT)^{3/2} l^3}{h^3}$$

$$= \frac{(2\pi mkT)^{3/2} V}{h^3}$$

$$\left(\frac{d \ln f}{dT}\right)_V = \frac{3}{2T}. \qquad\qquad E_{tr} = \frac{3}{2} NkT.$$

$$\left(\frac{d \ln f}{dV}\right)_V = \frac{1}{V} \qquad\qquad P = \frac{NkT}{V}$$

N.B. For Ar at 300°K in 1 cc, $f_{trans} = 2.5 \times 10^{26}$. Since each term of the sum is < 1, there are > 10^{26} levels.

SACKUR-TETRODE EQUATION

$$S_m = N_o k \left[\frac{3}{2} \ln \left\{ \frac{2\pi mkT}{h^2} \right\} + \ln \frac{Ve}{N_o} + \frac{3}{2} \right]$$

since $PV = N_o kT$. $M = N_o \, m$.

$$S_m = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R\ln P - 9.7 \quad J \, mol^{-1} \, K^{-1}$$

for translation of any gas.

Internal Degrees of Freedom

Exclusion principle no longer relevant.

$$\varepsilon = \varepsilon_{trans.} + \varepsilon_{rot.} + \varepsilon_{vibr.}$$

These are independent (c.f. Born-Oppenheimer approximation)

$$f = f_{trans.} \times f_{rot.} \times f_{vibr.}$$

Rotation of a linear molecule

$$\varepsilon_J = \frac{h^2}{8\pi^2 I} \, J(J+1)$$

$$g_J = 2J + 1.$$

$$f_{rot.} = \sum_{J=0}^{J=\infty} (2J + 1) \exp \left[- \frac{h^2 J(J+1)}{8\pi^2 I kT} \right]$$

$$\simeq \int_0^\infty (\quad) \, dJ = \frac{8\pi^2 I kT}{\sigma \cdot h^2}$$

σ - rotational symmetry number.
This expression gives $E_R = N K T$, i.e. it includes both classical rotational degrees of freedom.

Non-Linear molecule

$$f_{rot} = \pi^{\frac{1}{2}} \frac{(8\pi^2 kT)^{\frac{3}{2}} I_A^{\frac{1}{2}} I_B^{\frac{1}{2}} I_C^{\frac{1}{2}}}{\sigma h^3}$$

This is a good approximation for many molecules.

Vibration

Simple Harmonic Oscillator.

$$= (n + \tfrac{1}{2}) h\nu \qquad\qquad g = 1.$$

$$f_v = \sum_{n=o}^{n=\infty} \exp\left[- \frac{(n+\tfrac{1}{2}) h\nu}{kT}\right]$$

$$= \frac{e^{\frac{-h\nu}{2kT}}}{1 - e^{\frac{-h\nu}{kT}}} ..$$

By convention, we choose the lowest vibrational level of a molecule as our energy zero, is that $= n h \nu$.

$$\text{Then } f_v = \frac{1}{1 - e^{\frac{-h\nu}{kT}}}.$$

For a polyatomic molecule, resultant f_v is product of individual f_v's.

If $h\nu \ll kT$ (which it NEVER is !)

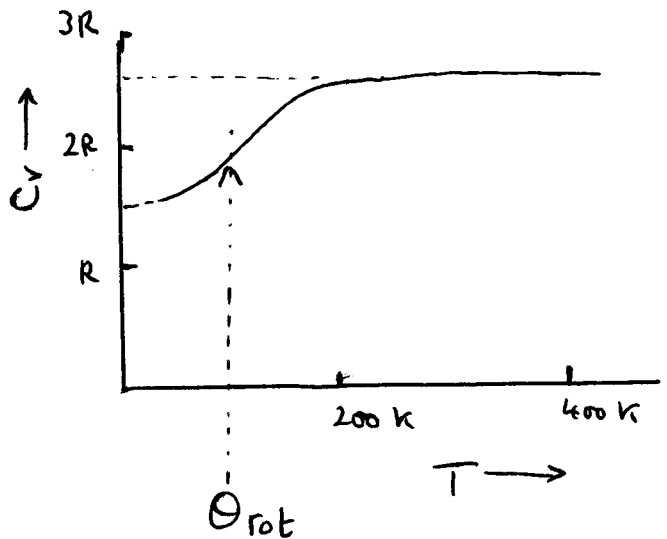$$f_v \rightarrow kT/h\nu; \text{ we call } h\nu/k = \Theta_{vib}$$

and the approximation would be true if $T \gg \Theta_{vib}$. Likewise we can define $\Theta_{rot} = h^2/8\pi^2 I k$

SOME VALUES:

Gas	Θ_{rot}	Θ_{vib}
	°K	
H$_2$	85.4	6,100
N$_2$	2.86	3,340
O$_2$	2.07	2,230
CO	2.77	3.070
NO	2.42	2,690
HCl	15.2	4,140
HBr	12.1	3,700
HI	9.0	3,200

Note effect on C_v

Symmetry problems for O_2, H_2, D_2, C_2H_2 etc.

Rotational levels.

$$\text{Fermi} - \text{Dirac}$$
$$\text{Bose} - \text{Einstein}$$

N.B. O - p. H_2 eq.

$$K_r = \frac{f''_o}{f''_p} \qquad \text{(no chemical terms)}$$

$$f''_o = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} \left[3 \sum_{J_{odd}} (2J+1) e^{-\frac{J(J+1) h^2}{8\pi^2 I kT}}\right] e^{-\frac{1}{2} h\nu/kT}$$

$$f''_p = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} \left[1 \sum_{J_{even}} (2J+1) e^{-\frac{J(J+1) h^2}{8\pi^2 I kT}}\right] e^{-\frac{1}{2} h\nu/kT}$$

At low temps, need take only 1st term for rot^n Sum

$$\frac{f''_o}{f'_p} = \frac{3 \times 3 e^{-2(h^r/8\pi^2 I kT)}}{1} = 9 e^{-2h^2/8\pi^2 I kT}$$

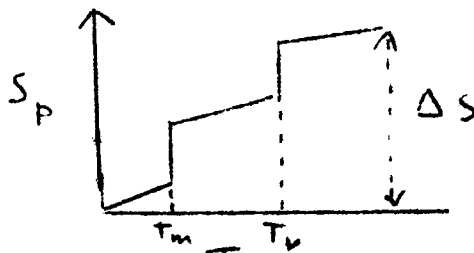at $10°K \sim 10^{-6}$, at $20°K \sim 2 \times 10^{-3}$

Third Law of Thermodynamics

Suggest that at $T = 0$, $S = 0, = k \log 1$ (ordered state)
$\therefore$ can calculate $S(T,V)$ from energy levels.

$$S(T, P) = S(T = 0, P) + \int_{T=0}^{T_m} \left(\frac{\partial S}{\partial T}\right)_P dT + \frac{\Delta H_m}{T_m} \quad \text{etc etc for } H_r$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$

We can compare S_{spec} with S_{calor} ($= S_{obs} - S_o$)

Sackur - Tetrode Equation. (for trans) : cf p

$$S_{trans} = -\left(\frac{\partial A_{trans}}{\partial T}\right)_V$$

Using the expressions for A trans, and $\int$ trans & PV = NkT, we get

$$S = Nk\left[\frac{5}{2}\ln T - \ln P + \ln\left\{\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}k^{\frac{5}{2}}\right\} + \frac{5}{2}\right]$$

e.g. H_2O :-

Spec		
S_{trans} = 145.02	J mol^{-1} $^{\circ}C^{-1}$	
S_{rot} = 43.91	" " "	
S_{vib} = 0.00	" " "	
188.93		

Polyatomic

$$f_{rot} = \frac{\sqrt{\pi}\,(8\pi^2 k T)^{\frac{3}{2}}\sqrt{I_A I_B I_c}}{\sigma \, h^3}$$

Calor	
Debye $\underline{T}^3$ extrap. to $10^{\circ}K$	= 0.09
Ice $10^{\circ}K \to 273.1^{\circ}K$	= 38.05
Melting at $273.1^{\circ}K$	= 22.02
$273.1^{\circ}K \to 373.1^{\circ}K$	= 6.62
Vap. at $373.1^{\circ}K$	= 147.57
Compression to 1 atm.	= -28.84
	185.51

fairly close agreement

$25^{\circ}C$ / 1atm.

Gas	S_{spec}	S_{calor}			$S_{spec} - S_{calor}$
HCl	187.0	186.5			
O_2	205.6	205.7			
Cl_2	223.4	223.4			
CO	198.2	193.6	x	outside	4.6
N_2O	220.3	215.5	x	error $S_o > o$ for some	4.8
H_2O	188.9	185.5	x	reason	3.4

Residual entropy = molecules barely distinguishable

$\therefore$ might be $= k \ln 2^N = k \ln 2$ at most

$$= 5.8 \; J \, mol^{-1} K^{-}$$

for CO, N_2O

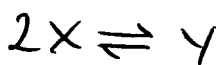H_2O crystal lattice not symmetrical

$$S_o = k \ln\left(\frac{3}{2}\right)^N$$
$$= R \ln \frac{3}{2} = 3.39 \; J \, mol^{-1} K^{-1} \;(!!)$$

Equilibrium
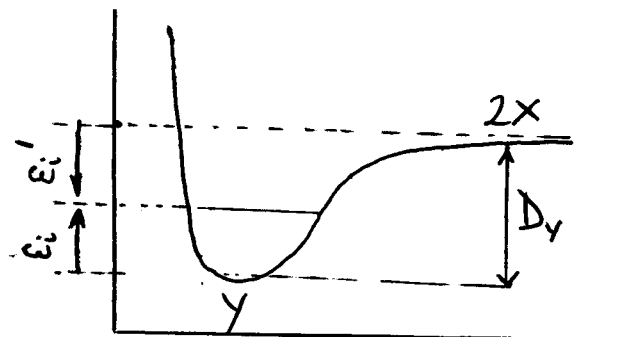
Take Dissociation as example

$$2X \rightleftharpoons Y$$

Note energy measurement from product state

$$\varepsilon_i' = \varepsilon_i - D_y$$

Thus $\quad f_Y' = \sum e^{-\mathcal{E}_i'/kT}$

$$= e^{D_Y/kT} \sum e^{-\mathcal{E}_i/kT}$$

$$= e^{D_Y/kT} \cdot f_Y$$

$$\mu_Y' = kT \ln (N_Y/f_Y') = kT \ln (N_Y/f_Y) - D_Y$$

CONSTANT VOLUME EQUILIBRIUM $\rightarrow$

$$\Delta A'_{T,V} = 0 = \left(\frac{\partial A'}{\partial N_Y}\right) \cdot 1 - \left(\frac{\partial A'}{\partial N_x}\right) \cdot 2$$

$$= \mu_Y' - 2\mu_x'$$

$$= \mu_Y - D_Y - 2\mu_x \qquad (\mu_x' = \mu_x)$$

$$= kT \ln (N_Y/f_Y) - D_Y - 2kT \ln (N_x/f_x)$$

$$\therefore \quad \frac{N_Y}{N_x^2} = \frac{f_Y}{f_x^2} e^{D_Y/kT}$$

NOTES

1) $\quad f = \left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} V \cdot f_{rot} \cdot f_{vib}$

We define $f'' = f/V$ (ie. volume independent)

Then

$$K_V = \frac{(N_Y/V)}{(N_x/V)^2} = \frac{f_Y''}{(f_x'')^2} e^{D_Y/kT} \left[= \frac{P_Y/kT}{(P_Y/kT)^2} \right]$$

And thence

$$K_P = \frac{1}{kT} \frac{f_Y''}{(f_x'')^2} e^{D_Y/kT}$$

2) Use of the equilibrium expressions in the Transition state theory of chemical kinetics