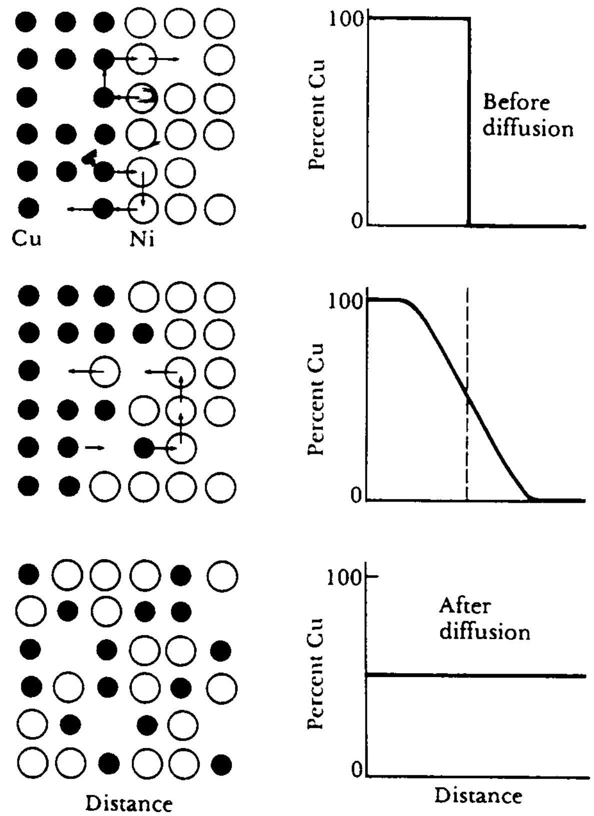
Diffusion

- Diffusion is the relative movement of atoms in a solid, liquid or gas □ we are concerned here with diffusion in **solids**.
- Is very important in

1. phase transformations
2. corrosion resistant coatings
3. separation of U_{235} by gaseous diffusion
4. permeability
5. impurity transistors
6. metal joining by diffusion bonding
7. **radiation damage / defects - defect migration**



Fick's 1st Law : (no time dependence)

$$\boxed{J = -D\frac{dc}{dx}}$$

$\{ = -D\ \nabla C$ in 3-dimensions$\}$

$[J] = \#/cm^2 s \quad [C] = \#/cc \quad [D] = cm^2/s$

- note - J along **negative** concentration gradient

$$J_1 - J_2 = \left(\frac{\partial C}{\partial t}\right)\Delta x = -\frac{\partial J}{\partial x}\Delta x$$

$$\text{or}\ \frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = -\frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right) = D\frac{\partial^2 C}{\partial x^2},$$

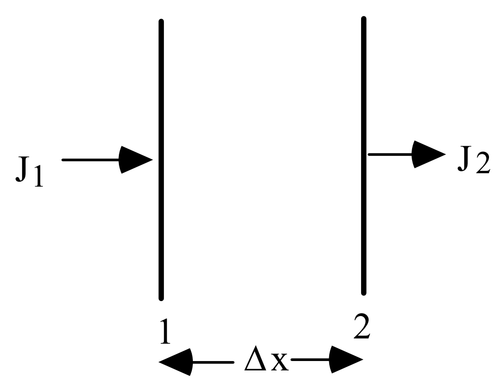
if $D \neq f(x)$ which is true for most cases:

$$\boxed{\frac{\partial C}{\partial t} = D\nabla^2 C} \quad \Rightarrow \text{diffusion eqn.}$$

Find the general and particular solutions $\{C(x,t)\}$ to the diffusion equation using initial and boundary conditions.

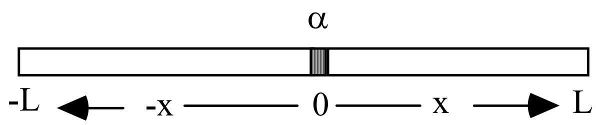
Fick's 2nd Law : C + f(x,t)

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$



Examples

1. Thin-film solution {find $C(x,t)$}



α is the amount in the **thin** layer at x=0 and L is very large

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

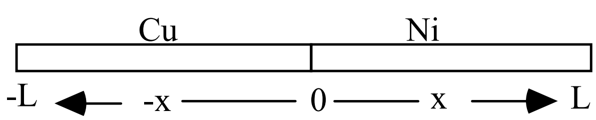
$$\& \quad \begin{matrix} x = 0 \;\; C \to \infty \text{ as } t \to 0 \\ |x| > 0 \;\; C \to 0 \text{ as } t \to 0 \end{matrix}$$

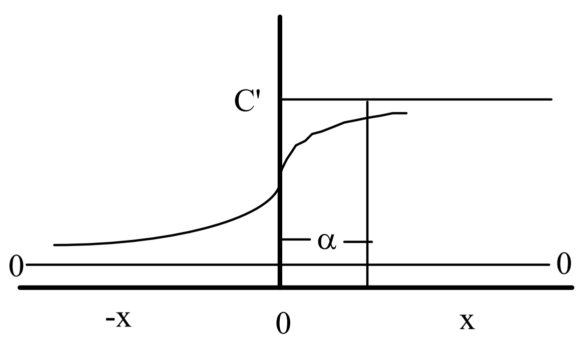
note $C = A\exp(-\frac{x^2}{4Dt})$ satisfies the above equation

A is defined by $\int_{-\infty}^{+\infty} C(x,t)dx = \alpha$

$$\therefore C = \frac{\alpha}{2\sqrt{\pi Dt}}\exp(-\frac{x^2}{4Dt})$$

2. Pair of semi-infinite solids

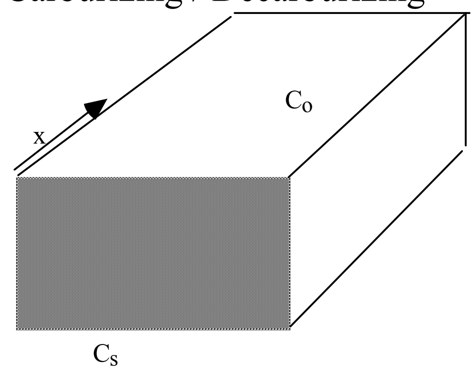




$$C(x,t) = \frac{C'}{2\sqrt{\pi Dt}}\int_0^{\infty}\exp(-\frac{(x-\alpha)^2}{4Dt})d\alpha$$

$$C(x,t) = \frac{C'}{2}\left[1 + \text{erf}(\frac{x}{2\sqrt{Dt}}\right]$$

3. Carburizing / Decarburizing



Solution

$$\boxed{\frac{C_s - C_x}{C_s - C_o} = \text{erf}(\frac{x}{2\sqrt{Dt}})}$$

$$\begin{cases} C_0 = \text{initial concentration} \\ C_s = \text{surface concentration} \end{cases}$$

for $t = 0$, $C = C_o$ at $o \le x \le \infty$

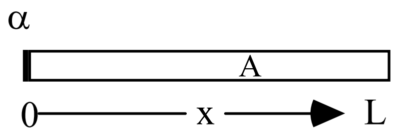
for $t > o$, $C = C_s$ (constant) at $x = 0$

and $C = C_o$ at $x = \infty$

where $$\boxed{\text{erf}(x) = \frac{2}{\sqrt{\pi}}\int_o^x \exp(-\xi^2)\, d\xi}$$

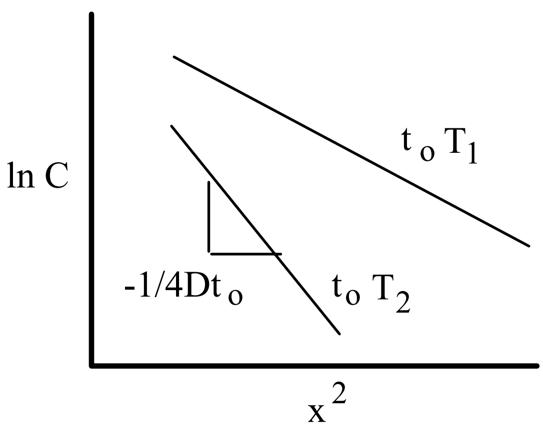
$$\begin{cases} \text{erf}(0) = 0 \\ \text{erf}(\infty) = 1 \\ \text{erf}(x) = \text{erf}(-x) \end{cases}$$

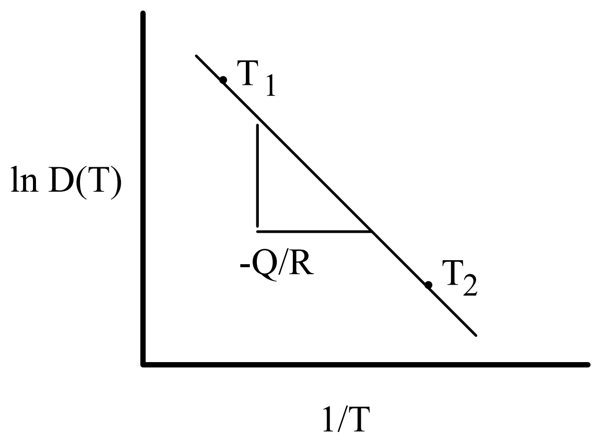
4. Diffusion Experiment (self diffusion)



α is the radioisotope of the metal A

$$C = \frac{\alpha}{2\sqrt{\pi D t}} \exp(-\frac{x^2}{4Dt})$$





$$D = D_o \exp(-\frac{Q_D}{RT})$$

Mechanism (?)

Atomic Theory of Diffusion

{Ref. Paul Shewmon, *Diffusion in Solids* , 2nd edition, TMS, 1989}

D $\Rightarrow$ atomic jump distance & frequency $\Leftrightarrow$ random walk theory (text, Eq.7.25)

Another way to do this is (see notes) : (no specific micromechanism !)

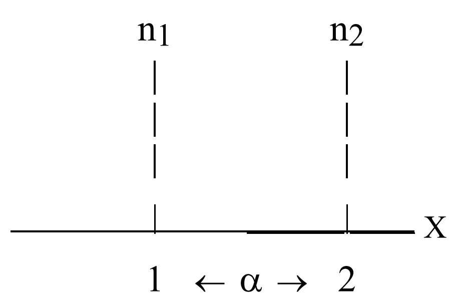
Consider two adjacent crystal lattice planes 1 and 2 [Fig.] separated by α.

{if the planes are {110} type $\alpha = \frac{a}{\sqrt{2}}$ since the direction x then is <110> type}

n_1, n_2 : no. of atoms / unit area

Γ = number of jumps they make per sec.

$\frac{1}{2}\, n_1\, \Gamma\, \delta t$ is the number jumping from plane 1 to plane 2



The atoms cannot stay in-between since there is no lattice plane between 1 and 2

The flux of atoms crossing a plane between 1 and 2 [J] :

$$J = \frac{1}{2}\,(n_1 - n_2)\,\Gamma = \frac{\text{number of atoms}}{\text{(area) (time)}} \quad .$$

In terms of the concentrations [c, per unit volume] : $c_1\alpha = n_1$ and $c_2\alpha = n_2$

$$J = \frac{1}{2}\,(c_1 - c_2)\,\alpha\,\Gamma \quad \text{or} \quad J = \frac{1}{2}\,\left\{-\alpha\frac{dc}{dx}\right\}\alpha\,\Gamma$$

Recalling Fick's first law $\{J = - D\,\frac{dc}{dx}\}$, $D = \frac{1}{2}\,\alpha^2\,\Gamma$ or $\boxed{D = \frac{1}{6}\alpha^2\,\Gamma}$

This equation is similar to the one derived in the text using random-walk theory,

$\overline{r^2} = \Gamma\, t\, \alpha^2$ (Eq.7.17) and also $\overline{r^2} = 6\, D\, t$ (Eq.7.24), so that $D = \frac{1}{6}\,\alpha^2\,\Gamma$

• note : no specific mechanisms of atom jumping assumed •

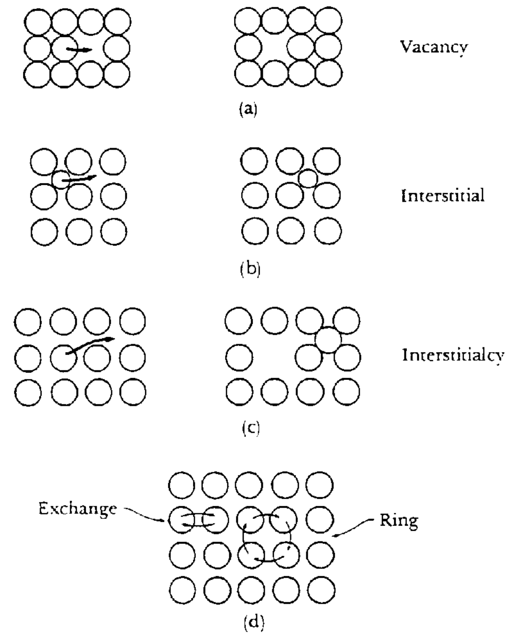
Diffusion Mechanisms

Vacancy

Interstitial

Interstitialcy

Ring

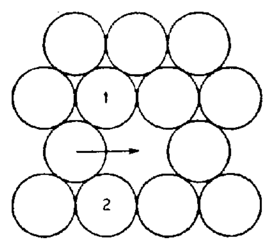


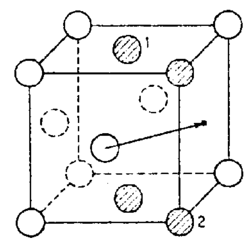
Self-diffusion via Vacancy Mechanism

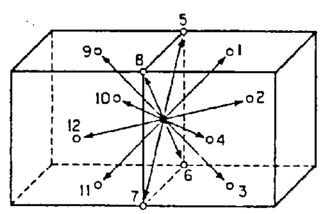
Γ is proportional to the number of nearest neighbors [β] and the probability of finding the lattice point vacant, i.e., the vacancy concentration [C_V] so that

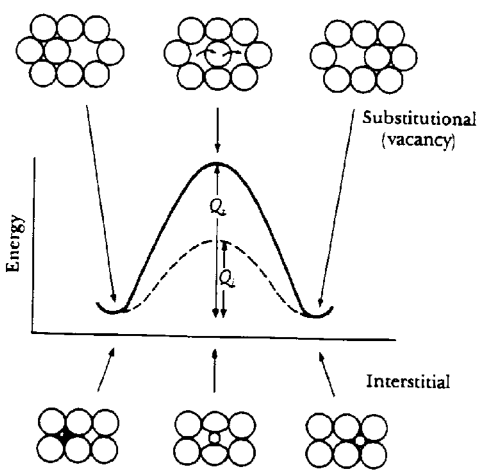
$$\Gamma = \beta\, C_V\, \omega,$$

where ω is the atomic jump frequency, $\omega = \nu_D\, e^{-(E_m / kT)}$









$$\therefore\ D = \frac{1}{6}\ \alpha^2\ \Gamma = \frac{1}{6}\ \alpha^2\, \beta\, C_V\, \nu_D\, e^{-(E_m/kT)}$$

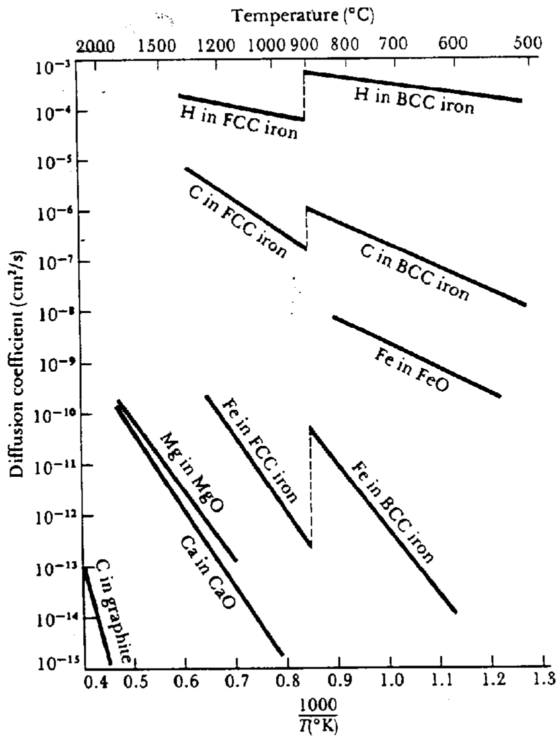
$$C_V = e^{-(E_f / kT)}$$

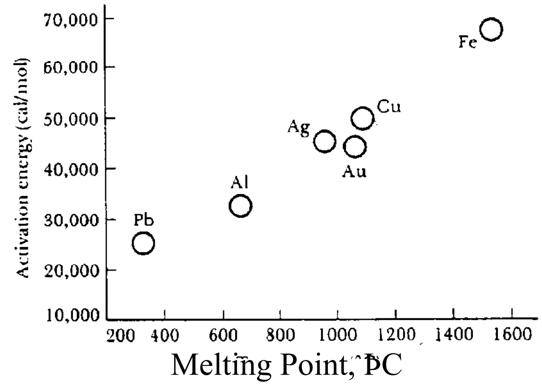
$$D = \frac{\beta}{6}\ \alpha^2\, \nu_D\, e^{-(E_m/ kT)}\, e^{-(E_f / kT)}$$

• For diffusion of vacancies, there is no need for C_V and only E_m appears in the expression for D_V •

Or $\boxed{D_L = D_{SD} = \frac{z}{6}\ \alpha^2\, \nu_D\, e^{-(E_D/ kT)} = D_o^L\, e^{-(E_D/ kT)}}$, $\boxed{E_D = E_f + E_m}$

$\Rightarrow$ similarly for interstitial diffusion : $D_i = D_o^i \, e^{-(E_m^i/kT)}$

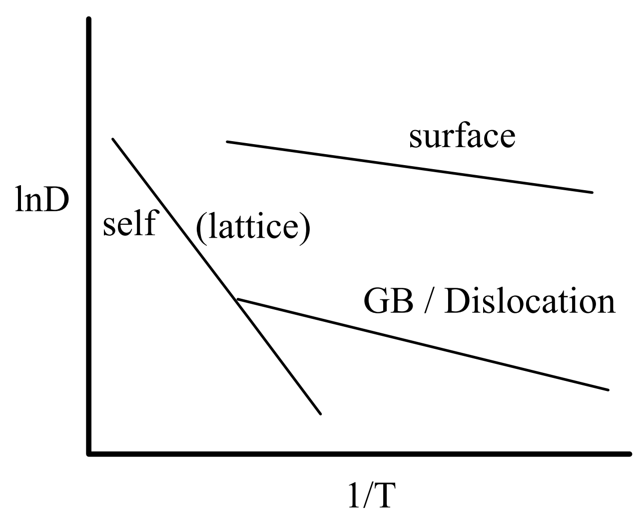




Short-Circuit Diffusion

- Surface ($Q_S < Q_D$)
- Grain-Boundary ($Q_{GB} < Q_D$)
- Dislocations (Pipe) ($Q_{GB} \approx Q_{\perp}$)

$Q_{GB} \approx 0.35\, Q_D$

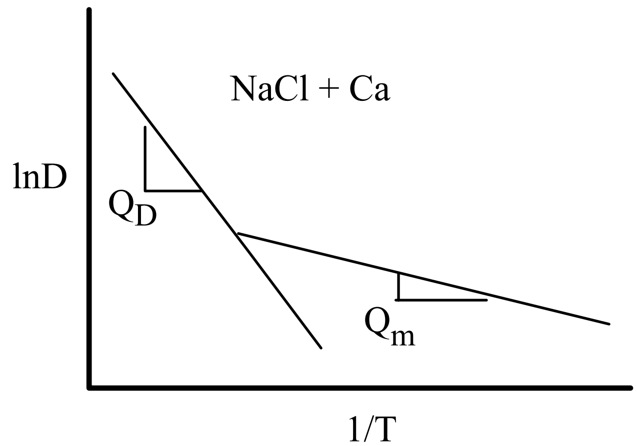


Diffusion in Ionics

e.g. Schottky-type : $E_D = E_m + \frac{1}{2} E_s$

NaCl with Ca^{++}

at low temperatures, where extrinsic vacancies dominate, $E_D = E_m \Leftarrow$ vacancy concentration is *independent* of temperature (athermal vacancies)
$\Rightarrow$ thus can determine both E_s and E_m



In metals, it is not easy to determine E_f and E_m separately -

1. Can get E_f from (a) Simmons-Balluffi experiment,

   or (b) Quenched in Resistivity

2. Annealing of quenched-in vacancies $\Rightarrow E_m$

Quench from high temperature ,
determine $\Delta\rho_o$; heat to T for t ; quench and determine $\Delta\rho$

$\Delta\rho\,(t) = \Delta\rho_o\, e^{-t/\tau}$ where $\tau(T)$ is the time for a vacancy to anneal out to sink

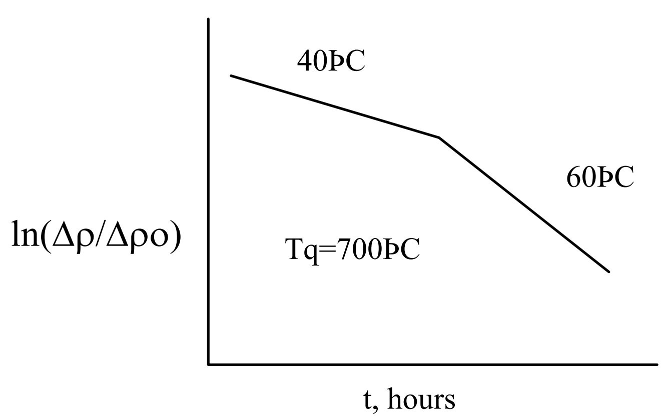
$\tau \propto \frac{l^2}{D_v}$ where l is the sink distance and $D_v \propto e^{-E_m/kT}$

{note : $D_v = \frac{\beta}{6}\,\alpha^2\, e^{-Em/kT}$ no C_v appears since T is low enough thta the quenched-in vacancies from 'high' temperature is far larger}

Example : Bauerle & Koehler in Au

$$\frac{\tau_1}{\tau_2} = \frac{D_v(T_2)}{D_v(T_1)} = \exp\{-\frac{E_m}{k}(\frac{1}{T_2} - \frac{1}{T_1})\}$$

$E_m = 0.82$ eV (18.9 kCal/mole)



Group Work *(solutions)*

For the example below, determine
(a) β and α (in cm), and (b) lattice diffusivity, D_L in cm^2/s at 500 ˚C.*

$$D_L = \frac{\beta}{2\,D}\,\alpha^2\,\nu_D \exp\left(-\frac{Q_D}{RT}\right),$$

β = no. of positions an atom can jump to,
and D in the denominator is the dimension (1, 2 or 3)

Group 1. for Cu (fcc) along <110> : $\beta = 12$, $\alpha = \frac{a}{\sqrt{2}} = 2.556\text{x}10^{-8}$ cm,

$$D_L = \frac{12}{6}(2.556\text{x}10^{-8})^2\,10^{13}\exp\left(-\frac{50000}{1.987\text{x}773}\right) = 9.547\text{x}10^{-17}\ cm^2/sec$$

Group 2. for Cu (fcc) along <100> : $\beta = 6$, $\alpha = a = 3.615\text{x}10^{-8}$ cm

$$D_L = \frac{6}{6}(3.615\text{x}10^{-8})^2\,10^{13}\exp\left(-\frac{50000}{1.987\text{x}773}\right) = 9.519\text{x}10^{-17}\ cm^2/sec$$

Group 3. for Cu (fcc) along <111> : $\beta = 8$, $\alpha = \frac{\sqrt{3}}{2}\,a = 3.131\text{x}10^{-8}$ cm

$$D_L = \frac{8}{6}(3.131\text{x}10^{-8})^2\,10^{13}\exp\left(-\frac{50000}{1.987\text{x}773}\right) = 9.521\text{x}10^{-17}\ cm^2/sec$$

Group 4. for Zr (hcp) along c-axis :

$\beta = 2$, $\alpha = c = 1.593\text{x}3.231$ Å $= 5.147\text{x}10^{-8}$ cm

$$D_L = \frac{2}{\mathbf{2}}(5.147\text{x}10^{-8})^2\,10^{13}\exp\left(-\frac{70000}{1.987\text{x}773}\right) = 4.270\text{x}10^{-22}\ cm^2/sec$$

note ‘2’ in the denominator - since the atom jumps are 1-D (!)

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* Cu : fcc, a = 3.615 Å, Q_D = 50 kCal/mole $\nu_D = 10^{13}$ per sec
Zr : hcp, a = 3.231Å, c/a = 1.593, Q_D^c = 70 kCal/mole, Q_D^a = 60 kCal/mole