# From Arrhenius to Vacancy Formation: Xtra Notes

We began with the general Arrhenius relation. Many phenomena depend not just on energy but on the energy of some process **relative** to thermal energy. When the process is "thermally activated" the Arrhenius relationship can describe its rate.

Rate (how often the process occurs in time)

Activation energy for process to occur

$$K = A * e^{-(Ea/RT)}$$

Average thermal kinetic energy

Pre-exponential (also called "frequency factor")

**Some things:**

1) if the Ea is per mole use the gas constant R (8.314 J/mol*K), if it's per atom use the Boltzmann constant $K_B$ ($8.62 \times 10^{-5}$ eV/K)
2) The pre-exponential factor A is related to how the process is attempted (we learn about it more later when we do reaction rates)
3) Ea is the energy required to "activate" the process. It's also known as the barrier height for a standard reaction coordinate vs. Energy plot.
4) The units of K and A must be the same, as with Ea and RT (or $K_BT$).

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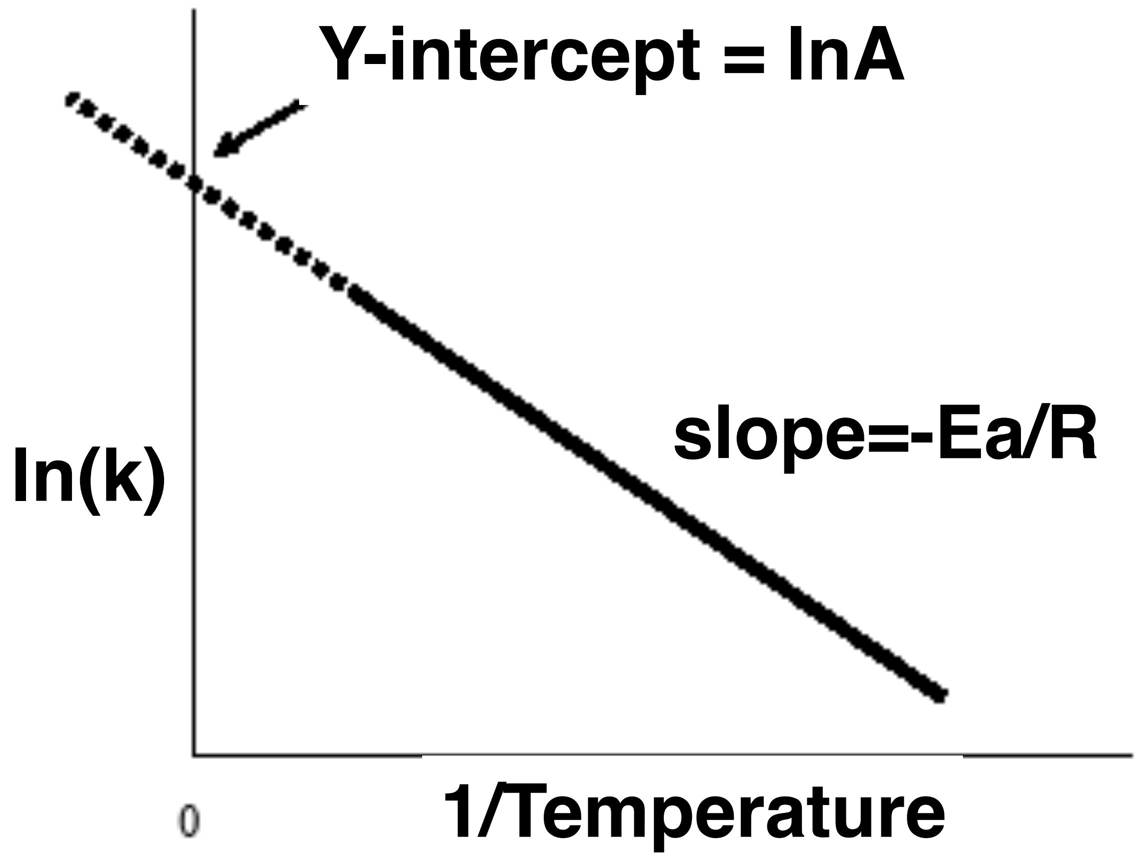
$$K=A*e^{-(Ea/RT)} \longrightarrow \ln(K)=\ln(A)-Ea/RT$$

**Take the log of the Arrhenius equation and we get a nice linear relationship between ln(K) and 1/T, like this:**

## Some things:

1) This is sometimes called an "Arrhenius plot," showing the inverse relation between reaction rates and temperature
2) The negative slope gives the activation energy, Ea: slope = -Ea/R
3) Extrapolation of the Arrhenius plot back to the y-intercept gives ln(A)
4) This plot shows how activation energy and temperature affect the sensitivity of the reaction rate



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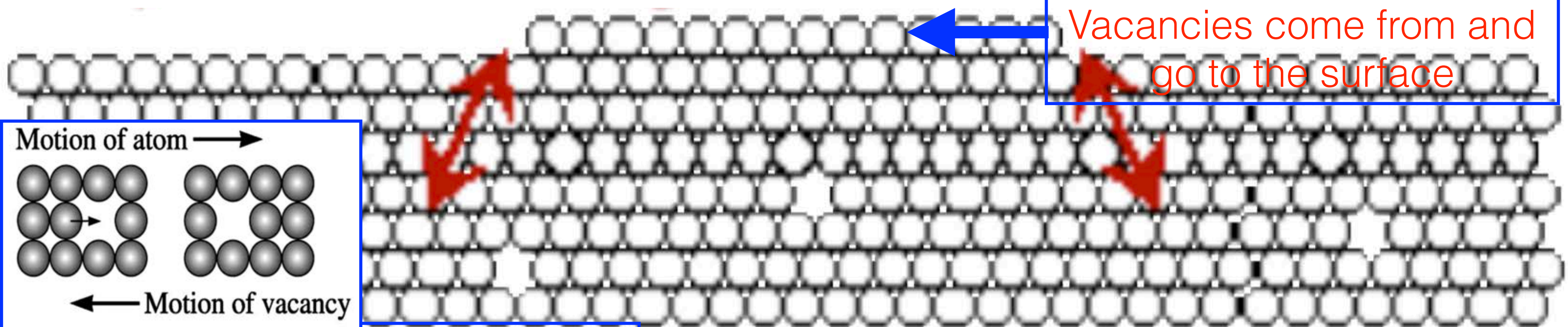
Next we related a thermally activated process to vacancy formation. A vacancy is formed by a surface atom moving up and creating room for the vacancy. Likewise a vacancy can “un-form” (or as it’s also called, annihilate).




Vacancies come from and go to the surface

Example of vacancy moving by one atomic position

The forming (call it rate 1) and un-forming (call it rate 2) of vacancies are both thermally activated processes:

$$K_1=A_1*e^{-(Ea1/RT)} \qquad K_2=A_2*e^{-(Ea2/RT)}$$

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$$K_1 = A_1 * e^{-(Ea1/RT)} \qquad K_2 = A_2 * e^{-(Ea2/RT)}$$

- The simplest rate has units 1/s. Then the flux of vacancies that form or un-form must multiply this rate by the number we have.
- **Flux of vacancies that form** = number of sites N that could form vacancies times the rate of forming vacancies K1
- **Flux of vacancies that un-form** = number of sites $N_V$ that could un-form vacancies times the rate of un-forming vacancies K2
- The system is in equilibrium (meaning the number of vacancies doesn't change) when the flux of forming vacancies is equal to the flux of un-forming vacancies.
- In other words, $N*K1 = N_V*K2$ —> $N_V/N = K1/K2$
- And we have now an expression for the vacancy concentration in equilibrium!

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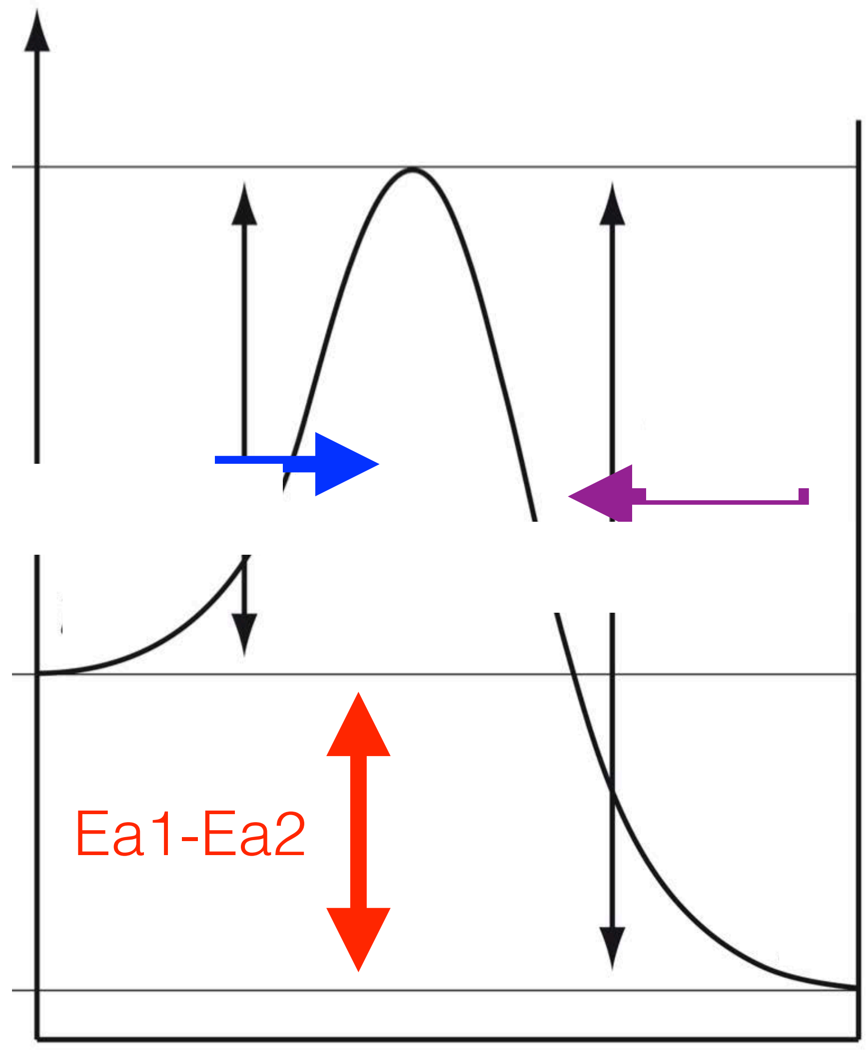
- Note that N is the number of sites that have an atom occupying them but could become a vacancy. But we just let this = to the number of lattice sites since that's a good approximation (it's much much larger than $N_V$).
- Do a little math and we get:

$$N_V/N=(A_1/A_2)^*e^{-((Ea1-Ea2)/RT}$$

We assume the frequency factors are roughly the same, and finally get:

$$N_V/N=e^{-Ev/RT}$$

Where Ev is the vacancy formation energy that is sometimes called Ev, and other times Qv, and other times (incorrectly) Ea



# From Arrhenius to Vacancy Formation: Xtra Notes

$$N_V/N = e^{-E_V/RT}$$

- This is the key equation you should know related to vacancy concentration
- So why did I show you all that general Arrhenius stuff?
- Because 1) that's where this relation for vacancies comes from, and 2) you'll need to know about Arrhenius for other topics so good to lay the groundwork here.

- for vacancy

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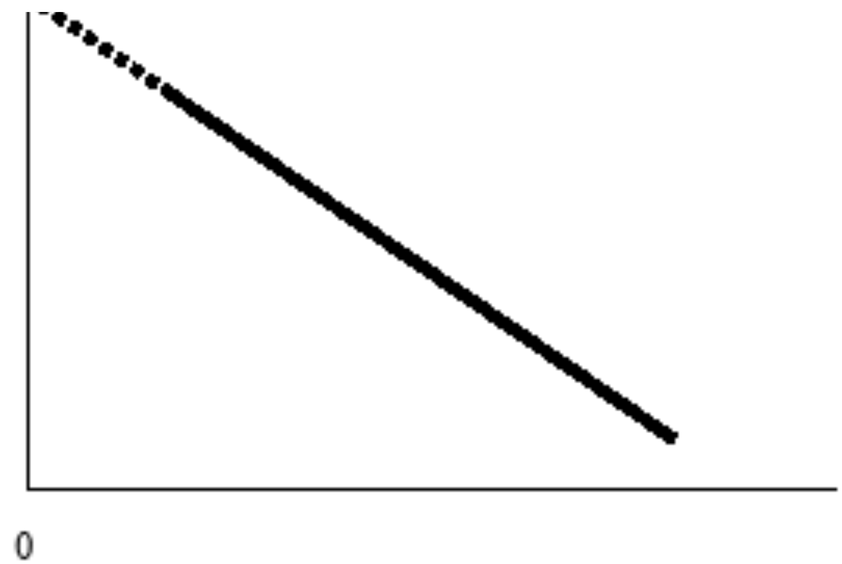


Remember that N is the number of possible vacancy sites (that's just the number of atoms!) and Nv is the number of vacancies. Ev is the vacancy formation energy: per mole use R, per atom use $K_B$.