Problem 9.1 – Arrhenius Behavior

A system’s energy is shown schematically in the upper figure at the right. The system is represented by the dot, which sits near the bottom of a local energy minimum. Over a peak in the energy lies a global energy minimum, which is where the system “wants” to be for maximum stability. To pass over the peak the system must raise its energy by \( E \) above the local minimum, after which it falls readily into the global minimum. The system might be an electron-hole pair in a semiconductor, in which case the low-energy state could correspond to the electron and hole recombining to emit a visible photon, although the situation is quite common and describes a great many important systems. We can learn about the energy function by measuring the dependence of the decay rate on the temperature of the surroundings.

Frequently there is a “characteristic time” \( \tau \) over which the system’s energy can be expected to change. If the system were an oscillator, this time would be approximately its period. In a solid or molecule, it is roughly the vibration period.

On a time scale short compared to \( \tau \) the system’s energy is approximately constant. Once each time interval \( \tau \), on average, the system’s energy is “randomized.” Equivalently, once each time interval \( \tau \) the system tries to overcome the barrier, so that the attempt frequency is \( \gamma = \tau^{-1} \).

(a) Assuming that the probability of finding the system at energy \( \epsilon \) is proportional to the Boltzmann factor, and that the system attempts to overcome the barrier with frequency \( \gamma \), show that the average transition rate may be expressed

\[
W \propto \gamma \exp\left(-\frac{E}{k_B T}\right)
\]

(b) The lower figure plots the transition rate as a function of inverse temperature. From the plot and/or data shown, determine approximately the attempt frequency and the barrier height. You may use Kaleidagraph, Origin, or some other fitting software if you wish.
Problem 9.2 – Ideal Gas Averages (Reif 7.19) A gas of molecules, each of mass $m$, is in thermal equilibrium at the absolute temperature $T$. Denote the velocity of a molecule by $\vec{v}$, its three cartesian components by $v_x$, $v_y$, and $v_z$, and its speed by $v$. What are the following mean values:

(a) $\overline{v_x}$
(b) $\overline{v_x^2}$
(c) $\overline{v_x^2}$
(d) $\overline{v_x^3}$
(e) $(v_x + bv_y)^2$ where $b$ is a constant
(f) $\overline{v_x^2 v_y^2}$

Reif adds the following endearing remark: If you need to calculate explicitly any integrals in this problem, you are the kind of person who likes to turn cranks but does not think.
Problem 9.3 – Maxwellian Distribution

(a) What is the standard deviation (width) of the Maxwellian distribution of speeds of a classical gas in equilibrium at temperature $T$? That is, what is $\sqrt{\langle (v - \langle v \rangle)^2 \rangle}$?

(b) What is the width of the speed distribution of the atoms that emerge through a small hole in the wall of an oven maintained at $T$?

(c) In which of the two previous situations is the relative width of the distribution greater? The relative width is the ratio of the width to the average speed.