

Let's define $\lambda \equiv \exp(\mu/\tau)$ KK Eq. 5.60

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Lambda is called the (thermodynamic) absolute activity.

Remember that for an ideal gas, $\mu = \tau \ln(n/n_Q) = \tau \ln(p/p_Q)$ KK Eq. 5.12

$$\text{then, } \lambda = \exp[\tau \ln(n/n_Q)/\tau] = \exp[\tau \ln(p/p_Q)/\tau]$$

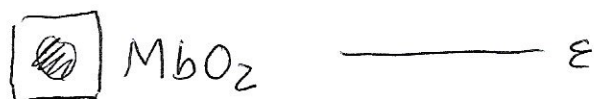
$$\lambda = \exp[\ln(n/n_Q)] = n/n_Q$$

$$\lambda = \exp[\ln(p/p_Q)] = p/p_Q \quad \text{KK Eq. 5.68}$$

So the absolute activity is something you can measure in the lab, since the concentration n , pressure p , and temperature τ are measurable.

Example: Occupancy zero or one (pg. 140)

A "red-blooded" example of a system occupied by zero or one molecule is the heme group, which can be occupied by zero or one O_2 molecules. The protein myoglobin has a single heme group, it is responsible for the red color of meat and allows whales and seals to spend a lot of time underwater.



Since energy must be supplied to MbO_2 to separate the Mb and O_2 , ϵ will be negative.

$$\langle N \rangle = \sum_{ASN} \frac{N \exp[(N\mu - \epsilon_s)/\tau]}{Z}$$

$$Z = \sum_{ASN} \exp[(N\mu - \epsilon_s)/\tau] = \sum_{ASN} e^{N\mu/\tau} e^{-\epsilon_s/\tau}$$

$$Z = \sum_{ASN} \lambda^N \exp(-\epsilon_s/\tau) \quad \text{KK Eq. 5.61}$$

$$\text{but } \frac{d}{d\lambda} Z = \frac{d}{d\lambda} \sum_{ASN} \lambda^N e^{-\epsilon_s/\tau} = \sum_{ASN} \frac{d}{d\lambda} \lambda^N e^{-\epsilon_s/\tau}$$

$$= \sum_s e^{-\epsilon_s/\tau} \sum_N \frac{d}{d\lambda} \lambda^N$$

$$= \sum_s e^{-\epsilon_s/\tau} \left[\frac{d}{d\lambda} \lambda^0 + \frac{d}{d\lambda} \lambda^1 + \frac{d}{d\lambda} \lambda^2 + \dots \right]$$

$$= \sum_s e^{-\epsilon_s/\tau} \left[0 + 1 + 2\lambda + 3\lambda^2 + \dots \right]$$

so

$$\lambda \frac{d}{d\lambda} Z = \sum_s e^{-\epsilon_s/\tau} \left[\lambda + 2\lambda^2 + 3\lambda^3 + \dots \right]$$

$$= \sum_s e^{-\epsilon_s/\tau} \sum_N N \lambda^N$$

$$= \sum_{ASN} N \lambda^N e^{-\epsilon_s/\tau} = \sum_{ASN} N \exp[(N\mu - \epsilon_s)/\tau]$$

Hence,

$$\langle N \rangle = \lambda \frac{1}{Z} \frac{d}{d\lambda} Z = \lambda \frac{d \ln Z}{d\lambda} \quad \text{KK Eq. 5.62}$$

For the zero or one occupancy case,

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$$N = 0, \quad \epsilon_{s(0)} = 0$$

$$N = 1 \quad \epsilon_{s(1)} = \epsilon.$$

$$\text{so } \mathcal{Z} = \lambda^0 e^{-0/\tau} + \lambda^1 e^{-\epsilon/\tau} = 1 + \lambda e^{-\epsilon/\tau} \quad \text{KK Eq. 5.66}$$

$$\langle N \rangle = \frac{\lambda}{\mathcal{Z}} \frac{d}{d\lambda} \mathcal{Z} = \frac{\lambda}{\mathcal{Z}} \left[0 + e^{-\epsilon/\tau} \right] = \frac{\lambda e^{-\epsilon/\tau}}{1 + \lambda e^{-\epsilon/\tau}} \quad \text{KK Eq. 5.69}$$

$$\langle N \rangle = \frac{\lambda e^{-\epsilon/\tau}}{\frac{\lambda e^{-\epsilon/\tau}}{1 + \lambda e^{-\epsilon/\tau}}} = \frac{1}{\lambda^{-1} e^{\epsilon/\tau} + 1} \quad \text{KK Eq. 5.69}$$

In Eq. 5.69, they call $\langle N \rangle = f$. You can interpret this as a "fraction." Assuming ideal gas behavior,

$$\langle N \rangle = f = \frac{\frac{1}{\tau n_Q} e^{\epsilon/\tau}}{\frac{1}{\tau n_Q} e^{\epsilon/\tau} + 1} = \frac{p}{\tau n_Q e^{\epsilon/\tau} + p} \quad \text{KK Eq. 5.70}$$

$$\text{Let } p_0 = \tau n_Q e^{\epsilon/\tau}, \text{ then } f = \frac{p}{p_0 + p} \quad \text{KK Eq. 5.71}$$

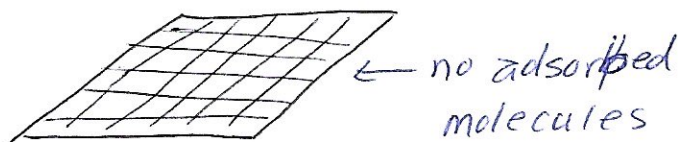
p_0 is a constant that depends on the temperature. With

$$p = n\tau, \quad f = \frac{1}{\frac{\tau n_Q}{n\tau} e^{\epsilon/\tau} + 1} = \frac{n}{n_Q e^{\epsilon/\tau} + n} \quad \leftarrow \text{this is the same functional form as the Fermi-Dirac distribution}$$

Let's check out the limiting behavior of the Langmuir adsorption isotherm.

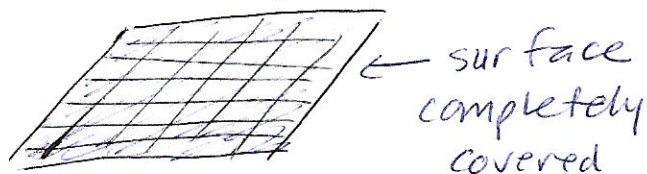
At very low concentration $n \ll n_Q$, $n \rightarrow 0$

$$f = \frac{0}{n_Q e^{\epsilon/k} + 0} = 0$$

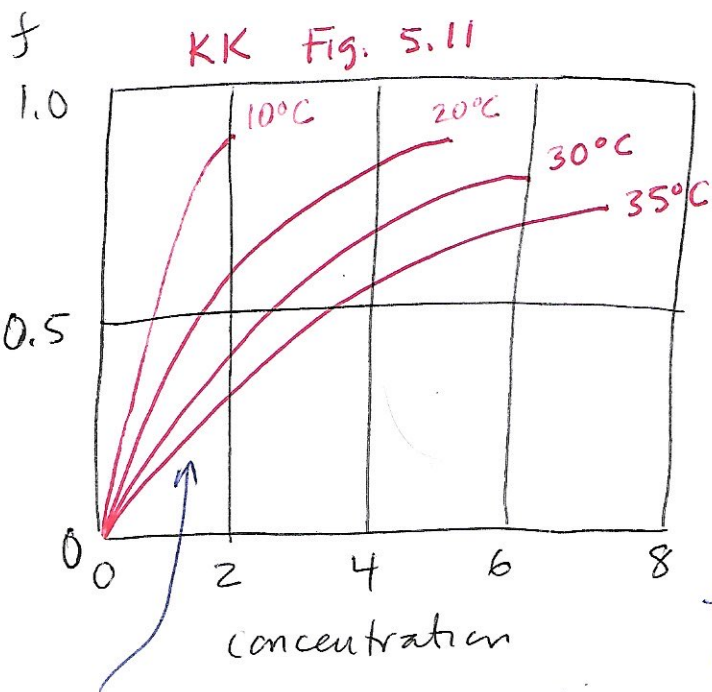


At very high concentration, $n \gg n_Q$, $n \rightarrow \infty$

$$f = \frac{n}{n} = 1$$



KK Fig. 5.11

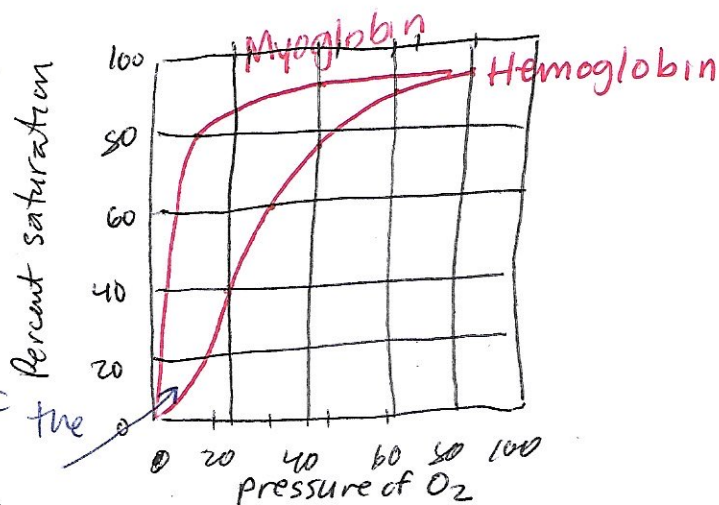


Adsorption of O_2 on myoglobin "surface"

At low temperature, O_2 molecules have less kinetic energy, so they are more likely to "stick" to myoglobin. At high concentration, more molecules per unit time "hit" the myoglobin, so higher chance of "sticking." Remember that myoglobin has negative binding energy.

By measuring the adsorption as a function of concentration for several temperatures it is possible to determine the relative chemical potential between gas and surface.

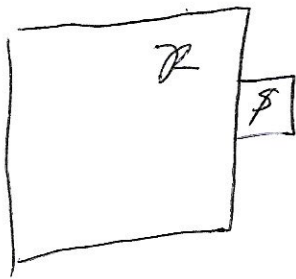
The curve of hemoglobin has a concave up part because adsorbing one oxygen changes the binding energy of the sites on the molecule (there are 4)



Example: Impurity atom ionization in a semiconductor (100)

In the conduction band of a semiconductor, the electron can move as a free particle. This is a "free electron gas".

The conduction band has many more electrons than the lone one that the impurity atom has to share, so the band acts like the reservoir and the impurity as the system.



Three states are available

- 1 Electron detached
- 2 " attached, spin up
- 3 " " , spin down

N	E
0	0
1	-I
1	-I

$$Z = \exp[(0\mu - 0)/\tau] + \exp[(1\mu + I)/\tau] + \exp[(1\mu + I)/\tau]$$

$$Z = 1 + 2 \exp[(\mu + I)/\tau] \quad \text{KK Eq. 5.72}$$

The probability that S is ionized (so no electron, $N=0$)

$$P(\text{ionized}) = P(0,0) = \frac{1}{Z} = \frac{1}{1 + 2 \exp[(\mu + I)/\tau]}$$

$$P(\text{neutral}) = P(\uparrow, -I) + P(\downarrow, -I) = 1 - P(\text{ionized})$$

Let's check out the limiting behavior

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In the high temperature limit $\tau \gg \mu + I$ $\tau \rightarrow \infty$

$$P(\text{ionized}) = \frac{1}{1 + 2 \exp[0/\infty]} = \frac{1}{3}$$

$$\text{So } P(\text{neutral}) = 2/3$$

The temperature is so high that electron does not "stick" anywhere, so the probability of finding it in any state is the same, although there are two neutral states.

In the low temperature limit $\tau \ll \mu + I$ $\tau \rightarrow 0$

$$P(\text{ionized}) = \frac{1}{1 + 2 \exp[\mu + I / 0]} = \frac{1}{\infty} = 0$$

$$\text{So } P(\text{neutral}) = 1$$

The temperature, so the kinetic energy of the electron, is so low that it can't escape the binding energy of the atom, so it can't be ionized.

In the low concentration limit $n \ll n_Q$ $\mu = \tau \ln(n/n_Q)$

$$P(\text{ionized}) = \frac{1}{1 + 2 \exp[\tau \ln(n/n_Q) / \tau]} = \frac{1}{1 + \frac{2n}{n_Q}} = \frac{n_Q}{n_Q + 2n} = \underline{\underline{1}}$$

$$\text{So } P(\text{neutral}) = 0$$

if the concentration of electrons in the conduction band is very low, there is a "vacuum" that will pull out the electron, so it will be ionized. Similarly for high concentration, $P(\text{ionized}) = 0$