CHAPTER 12: MEANING OF T

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

Consider Schottky two-state model

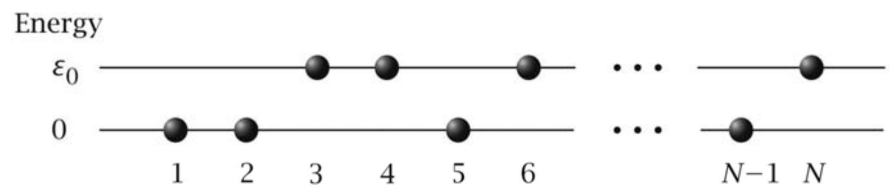
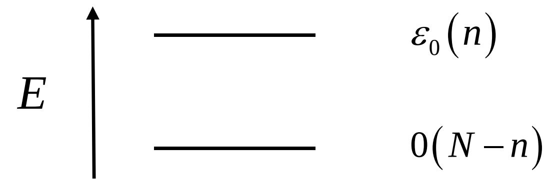


Figure 12.1 Molecular Driving Forces 2/e (© Garland Science 2011)



$$\langle \varepsilon \rangle = \frac{\varepsilon_0 e^{-\varepsilon_0/kT}}{1+e^{-\varepsilon_0/kT}} \qquad C_v = \frac{N\varepsilon_0^2}{kT^2}\frac{e^{-\beta\varepsilon_0}}{\left(1+e^{-\beta\varepsilon_0}\right)^2}$$

$$\downarrow$$

$$\frac{S}{N} = \frac{\varepsilon_0 e^{-\beta\varepsilon_0}}{T\left(1+e^{-\beta\varepsilon_0}\right)} + k\ell n\left(1+e^{-\beta\varepsilon_0}\right)$$

$$U = n\varepsilon_0 \rightarrow n = \frac{U}{\varepsilon_0}$$

$$W = \frac{N!}{n!(N-n)!}$$

$$\frac{S}{k} = \ell n W = -n \ell n \frac{n}{N} - (N-n)\ell n\left(\frac{N-n}{N}\right)$$

$$\frac{S}{k} = -\frac{U}{\varepsilon_0}\ell n\left(\frac{U}{N\varepsilon_0}\right) - \left(N - \frac{U}{\varepsilon_0}\right)\ell n\left(\frac{N - U/\varepsilon_0}{N}\right)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \left[\frac{1}{\varepsilon_0}\ell n\frac{U}{N\varepsilon_0} - \frac{U}{\varepsilon_0}\frac{1}{U} + \frac{1}{\varepsilon_0}\ell N\left(\frac{N - U/\varepsilon_0}{N}\right) - \left(N - \frac{U}{\varepsilon_0}\right)\frac{-1/\varepsilon_0}{N - U/\varepsilon_0}\right]k$$

$$\left[= \frac{1}{\varepsilon_0}\ell n\frac{n}{N} - \frac{1}{\varepsilon_0} + \frac{1}{\varepsilon_0}\left(\frac{N-n}{N}\right) - \frac{(N-n)(-1/\varepsilon_0)}{N-n}\right]k$$

$$= +\frac{1}{\varepsilon_0}\left[-1 - \ell n\frac{n}{N} + \ell n\frac{N-n}{N} + 1\right]k$$

$$= \frac{1}{\varepsilon_0}\left[\ell n\left(\frac{N-n}{N}\right) - \ell n\left(\frac{n}{N}\right)\right]k$$

$$= \frac{-k}{\varepsilon_0}\ell n\left(\frac{n/N}{(N-n/N)}\right) = \frac{k}{\varepsilon_0}\left(\frac{f_{ground}}{f_{excited}}\right)$$

| f = fraction

so *T* depends on $\varepsilon_0, \; N, \; U$

spacing of levels
particles
total energy

Now consider 3 particles in 2 levels

low $U, \rightarrow f_{ground} / f_{exc} > 1,$ so T positive

absorb energy to $> S$

if $f_{ground} = f_{excited}, \; 1/T = 0 \quad (T = \infty)$

$S(U)$ is at maximum

equal populations $\rightarrow T = \infty$

if more particles in upper level T is negative

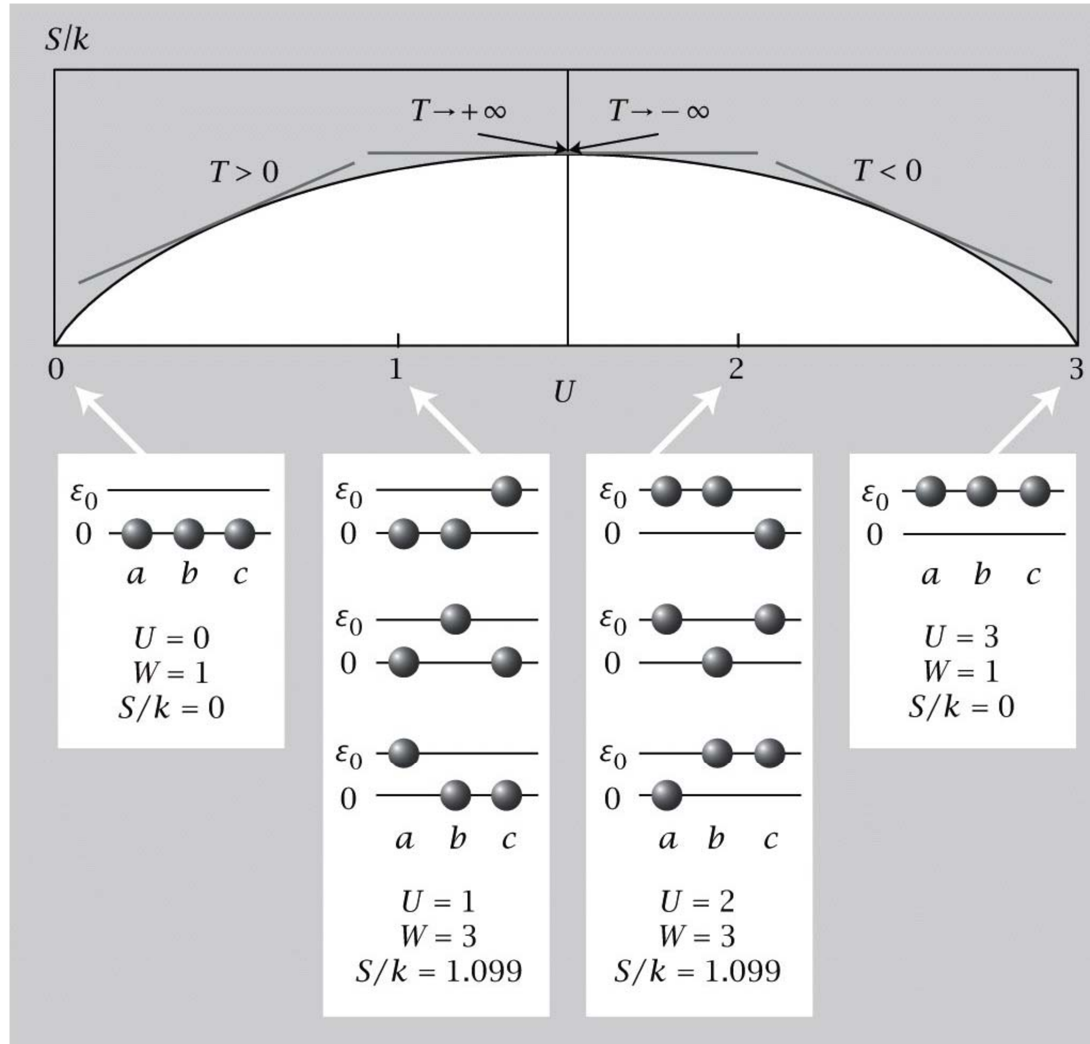


Figure 12.2 Molecular Driving Forces 2/e (© Garland Science 2011)

A system at $-T$ is hotter than at $+T$

This system would tend to give off energy, not to absorb it.

$$\frac{1}{T} > 0, \quad \text{system has tendency to absorb energy}$$

$$\frac{1}{T} < 0, \quad \text{system has tendency to lose energy}$$

Negative *T* only happens in systems with finite # levels and are saturable.

negative *T* systems ↔ population inversion

cannot be achieved by equilibrium with heat bath, since heat bath has +*T*

$dS = \frac{\delta q}{T}$: Reflection on this result

degrees of freedom *U, V, N,* hold *V, N* constant, so work = 0

$$\Rightarrow dU = \delta q$$

$dS = \frac{dU}{T} = \frac{\delta q}{T}$ system acquires heat from heat bath, due to increasing excited state population

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Ideal gas, *const V* $S = \frac{3Nk}{2} \ell n U$

$$S = 3/2Nk\ell n(U)$$ fixed *V, N*

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad U = 3/2NkT \quad T = 2/3U/Nk$$

$$dS = \frac{dU}{T} \qquad dS = \frac{NkdU}{2/3U} = 3/2Nk\frac{dU}{U}$$

$$\frac{1}{T_A} = \frac{1}{T_B} \Rightarrow \frac{1}{\varepsilon_A}\ell n\left(\frac{N_A\varepsilon_A}{U_A}\right) = \frac{1}{\varepsilon_B}\ell n\left(\frac{N_B\varepsilon_B}{U_B}\right)$$

same material $\varepsilon_A = \varepsilon_B$ and same # particles $N_A = N_B$, tendency to maximize *S* and to equalize temperatures is a tendency to equalize energies

if $\varepsilon_A = \varepsilon_B$ but $N_A \neq N_B$ then equilibrium when

$$\frac{N_A}{U_A} = \frac{N_B}{U_B}$$

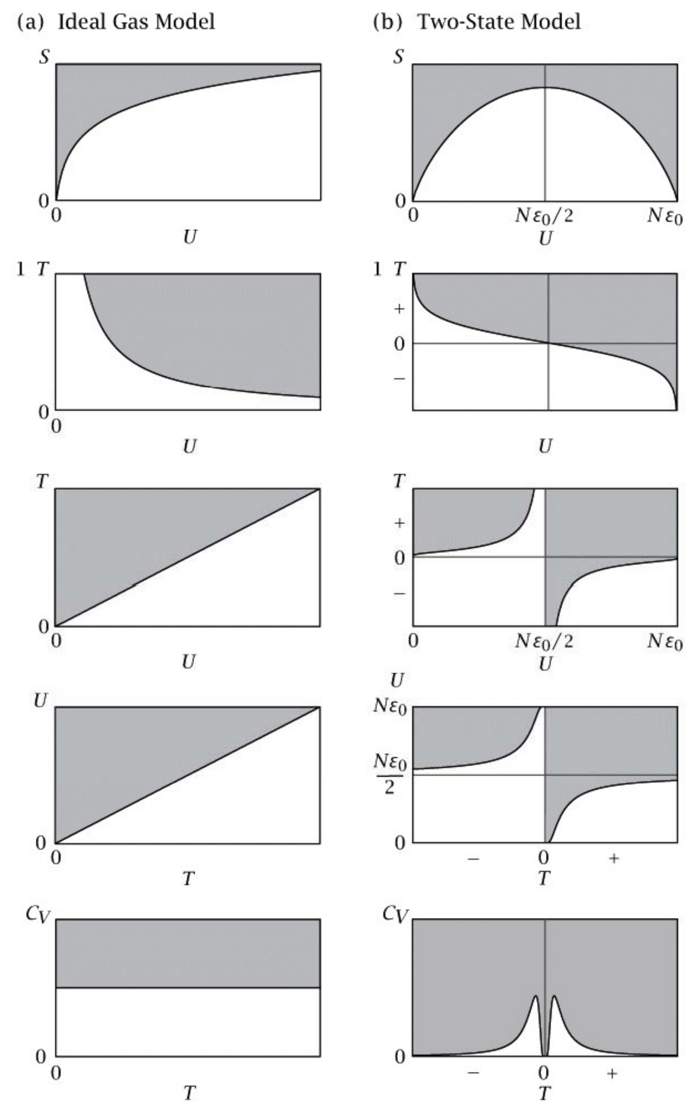

Figure 12.3 Molecular Driving Forces 2/e (© Garland Science 2011)

Heat capacity is a measure of energy fluctuations

$$p(E)=\frac{1}{2}W(E)e^{-\beta E}$$

Highly peaked
width determined by C_V

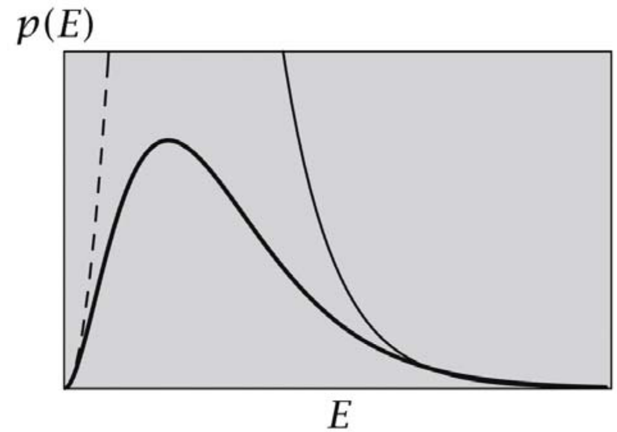

Figure 12.5 Molecular Driving Forces 2/e (© Garland Science 2011)

$$\ell np(E)=\ell np(U)+\left(\frac{\partial \ell np(E)}{\partial E}\right)_{E=U}(E-U)+\frac{1}{2}\left(\frac{\partial^2 \ell np(E)}{\partial E^2}\right)_{E=U}(E-U)^2$$

at peak $S(E)=S(U)$, equil. value

$$\frac{\partial \ell np(E)}{\partial E}=\frac{1}{kT(E)}-\frac{1}{kT_0}$$

$$\frac{\partial^2 \ell n(p(E))}{\partial E^2}=\frac{-1}{kT^2}\left(\frac{\partial T}{\partial E}\right)_{E=U}=-\left(\frac{1}{kT_0^2 C_V}\right)$$

$$p(E)=p(U)e\left[\frac{-(E-U)^2}{2kT^2C_V}\right]=e^{[U-T_0S(U)]}e^{-\frac{(E-U)^2}{2kT^2C_V}}$$

$$\Rightarrow \sigma^2=\left\langle (E-U)^2\right\rangle=\left\langle E^2\right\rangle-U^2=kT_0^2C_V$$

Ideal gas

$$\frac{\sigma}{U} = \frac{\sqrt{kT^2 C_v}}{3/2NkT} = \left(\frac{3}{2}N\right)^{-1/2}$$

$$N \sim 10^{23} \Rightarrow \frac{\sigma}{U} \sim 10^{-12}$$

Relatively speaking, the fluctuations are a very small amount of the total energy when N is large