5.62 Physical Chemistry II
Spring 2008

5.62 Lecture #3: Canonical Partition Function: Replace $\{P_i\}$ by Q

$$P_j = \frac{e^{-E_j/kT}}{\sum_m e^{-E_m/kT}} \quad \text{Canonical Distribution Function}$$

Denominator of canonical distribution function has a special name ...

$$Q(N,V,T) = \sum_j e^{-E_j/kT}$$

CANONICAL PARTITION FUNCTION

Sum of "Boltzmann factor", $e^{-E_j/kT}$, over states of the assembly

originally called "zustandsumme" ≡ Z ≡ sum over states

Q is a very very important quantity.

We will use Q to calculate macroscopic properties from microscopic properties

Rewrite Canonical Distribution Function in terms of Q ...

$$P_j = \frac{e^{-E_j/kT}}{\sum_m e^{-E_m/kT}} = \frac{e^{-E_j kT}}{Q}$$

FEEL THE POWER OF P_j — can now calculate macroscopic properties from ensemble average

... but more convenient to use Q.

REPLACING P_j IN ENSEMBLE AVERAGE BY Q

example: $\bar{E} = \sum_j P_j E_j = f(Q)$

Define $\beta \equiv 1/kT$

$$Q(N,V,T)=\sum_j e^{-E_j/kT}=\sum_j e^{-\beta E_j}$$

$$\frac{\partial Q}{\partial \beta}=-\sum_j E_j e^{-\beta E_j}$$

Now $$P_j=\frac{e^{-\beta E_j}}{Q} \quad \text{so} \quad e^{-\beta E_j}=QP_j$$

Therefore $$\frac{\partial Q}{\partial \beta}=-\sum_j P_j E_j Q=-Q\sum_j P_j E_j$$

But $$\bar{E}=\sum_j P_j E_j$$

So

$$\frac{\partial Q}{\partial \beta}=-\bar{E}Q \quad \text{or} \quad \bar{E}=-\frac{1}{Q}\frac{\partial Q}{\partial \beta}$$

$$\bar{E}=-\frac{1}{Q}\frac{\partial Q}{\partial \beta}=-\frac{\partial \ln Q}{\partial \beta}=-\frac{\partial \ln Q}{\partial (1/kT)}=-\frac{\partial \ln Q}{\partial T}\frac{\partial T}{\partial (1/kT)}$$

$$\bar{E}=kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}=kT^2\frac{\partial \ln Q}{\partial \ln T}\frac{\partial \ln T}{\partial T}=kT\frac{\partial \ln Q}{\partial \ln T}$$

This is the ensemble average for E written in terms of Q instead of P_j

Writing S in terms of Q instead of P_j

$$S=-k\sum_j P_j \ln P_j=-k\sum_j P_j \ln\left(\frac{e^{-E_j/kT}}{Q}\right)$$

$$S=-k\sum_j P_j\left[\frac{-E_j}{kT}-\ln Q\right]=\frac{\sum_j P_j E_j}{T}+k\ln Q$$

$$S=k\ln Q+\frac{\bar{E}}{T}=k\ln Q+k\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{N,V}$$

WRITING ALL THERMODYNAMIC FUNCTIONS OR MACROSCOPIC PROPERTIES IN TERMS OF Q

From thermo ...

$$A = \bar{E} - TS = \bar{E} - T\left(k \ln Q + \bar{E}/T\right) = \bar{E} - kT \ln Q - T\frac{\bar{E}}{T}$$

$$\boxed{A = -kT \ln Q} \qquad \text{Helmholtz free energy}$$

Note that both A and Q have natural variables N, V, T.

From thermo ...

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \qquad \text{pressure}$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

from thermo ...

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} \qquad \text{chemical potential}$$

(For μ, always natural variables held constant.)

$$\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

$$\left.\begin{matrix} H \equiv \bar{E} + pV \\ G \equiv A + pV \end{matrix}\right\} \text{ write in terms of Q in homework}$$

Now we have a rudimentary structure or framework for relating the microscopic properties as given by Q, the sum over states of assemblies present in the canonical ensemble, to macroscopic or thermodynamic properties. Note that Q (or P_j) tells us the distribution of assembly states present in the ensemble. We see that it is the energy of the state of the assembly that determines its probability of being in the ensemble. So now we need to know what are the energies of the assemblies, E_j, so that Q for specific systems may be calculated. Once Q is known, we can calculate all macroscopic thermodynamic properties from the above expressions!!

A LOOSE END: DEGENERACY — BACK TO P_j

Sometimes a more useful form of P_j is P(E).

GOAL: Derive P(E)

P(E) ≡ probability of finding an assembly state with energy E.

Each j in Q stands for a distinguishable state of the assembly.

$$Q=\ldots+e^{-E_\alpha/kT}+e^{-E_\beta/kT}+e^{-E_\gamma/kT}+\ldots=\sum_j e^{-E_j/kT}$$

But many distinguishable assembly states are <u>degenerate</u> (i.e. have the same energy)

$$E_\alpha = E_\beta = E_\gamma = E$$

$$Q=\ldots+\underset{\uparrow}{3}e^{-E/kT}+\ldots=\sum_E \Omega(N,V,E)\,e^{-E/kT}$$

$\Omega(N,V,E)$ ≡ degeneracy = no. of distinguishable assembly states with energy E.

So

$$Q(N,V,T)=\underset{\substack{j\\ \uparrow\\ \boxed{\text{sum over states of assemblies}}}}{\sum} e^{-E_j/kT}=\underset{\substack{E\\ \nwarrow\\ \boxed{\text{sum over energy levels present in ensemble}}}}{\sum}\Omega(N,V,E)e^{-E/kT}$$

$$P(E)=\sum_{j\ni E_j=E}P_j=\sum_{j\ni E_j=E}e^{-E_j/kT}\Big/Q(N,V,T)$$

Sum over those assembly states
that belong to the set of assembly states whose $E_j = E$

$$\boxed{P(E)=\frac{\Omega(N,V,E)e^{-E/kT}}{Q(N,V,T)}}$$

probability of finding an assembly state with energy E in ensemble