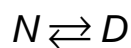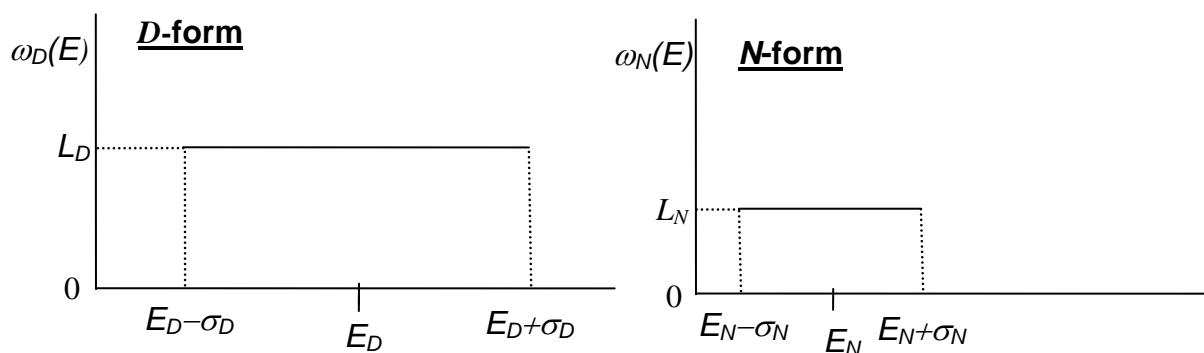**10.40 Thermodynamics**   **Fall 2003**

Final Exam

Problem 3

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3. (20 points) A protein system exists such that each protein molecule is either in its native form (*N*) or its denatured form (*D*). The *N* and *D* forms have different energy distributions (density of states) with the following structures:

$$N \rightleftarrows D$$

(a) (10 points) Explain under what circumstances you would expect the chemical equilibrium constant to follow the van't Hoff equation (ln *K* vs. $1/T$ is a straight line). Back up your explanation with appropriate numerical analysis.

(b) (10 points) Describe briefly using appropriate equations how the situation would differ for the gas phase equilibrium that we discussed in class:

$$H_2 + \tfrac{1}{2} O_2 = H_2O$$

Recall: the semi-classical canonical partition function Q_N is given by

$$Q_N = \int_{-\infty}^{\infty} e^{-E/kT} \omega(E) d(E)$$

where $\omega(E)$ is the density of energy states.

Solution:

(a)

The van't Hoff equation has the form: $\ln K = \dfrac{-\Delta H^o_{rxn}}{RT} + \dfrac{\Delta S^o_{rxn}}{R}$, where ΔH^o_{rxn} and ΔS^o_{rxn} are assumed to be constant.

Applying material learned during class lecture,

$$K_C(T) = \frac{Q_N^D}{Q_N^N} \tag{1}$$

$$Q_N^D = \int_{-\infty}^{\infty} e^{-E/kT}\,\omega(E)\,dE = \int_{E_D-\sigma_D}^{E_D+\sigma_D} e^{-E/kT} L_D\,dE$$

$$Q_N^D = -kTL_D\left\{e^{-(E_D+\sigma_D)/kT} - e^{-(E_D-\sigma_D)/kT}\right\} = -kTL_D e^{-E_D/kT}\left\{e^{-\sigma_D/kT} - e^{+\sigma_D/kT}\right\}$$

Similarly,

$$Q_N^N = -kTL_N e^{-E_N/kT}\left\{e^{-\sigma_N/kT} - e^{+\sigma_N/kT}\right\}$$

$$K_C(T) = \frac{Q_N^D}{Q_N^N} = \frac{-kTL_D e^{-E_D/kT}\left\{e^{-\sigma_D/kT} - e^{+\sigma_D/kT}\right\}}{-kTL_N e^{-E_N/kT}\left\{e^{-\sigma_N/kT} - e^{+\sigma_N/kT}\right\}}$$

Taking the natural log of K:

$$\ln K_C(T) = \ln\frac{Q_N^D}{Q_N^N} = \ln\frac{L_D}{L_N} - \frac{(E_D - E_N)}{kT} + \ln\left[\frac{\left\{e^{-\sigma_D/kT} - e^{+\sigma_D/kT}\right\}}{\left\{e^{-\sigma_N/kT} - e^{+\sigma_N/kT}\right\}}\right] \tag{2}$$

In order for the protein system to exhibit van't Hoff behavior, the bracketed term should not exhibit temperature dependence. There are two conditions that will fulfill this criterion.

1. $\sigma_D = \sigma_N$ Then numerator and the denominator of the bracketed term are the same and the $\ln(1) = 0$, so the term vanishes.

2. $\sigma_D, \sigma_N \ll kT$ This condition can be applied to a greater number of systems and is more likely to occur. The exponential terms can be expanded as a MacLaurin series that can be truncated after the second term.

$$\left[\frac{\left\{e^{-/kT} - e^{+\sigma_D/kT}\right\}}{\left\{e^{-\sigma_N/kT} - e^{+\sigma_N/kT}\right\}}\right] = \left[\frac{\left\{1 - \dfrac{\sigma_D}{kT} - \left(1 + \dfrac{\sigma_D}{kT}\right)\right\}}{\left\{1 - \dfrac{\sigma_N}{kT} - \left(1 + \dfrac{\sigma_N}{kT}\right)\right\}}\right] = \left[\frac{\left\{-\dfrac{2\sigma_D}{kT}\right\}}{\left\{-\dfrac{2\sigma_N}{kT}\right\}}\right] = \frac{\sigma_D}{\sigma_N} \tag{3}$$

Plugging Eq. (3) in (2) yields,

$$K_C(T) = \ln\frac{L_D}{L_N} - \frac{(E_D - E_N)}{kT} + \ln\left(\frac{\sigma_D}{\sigma_N}\right)$$

(4)

Eq. (4) follows van't Hoff behavior, since lnK vs. 1/T is a straight line.

(b)
All participants in the gas phase formation of water can be modeled as ideal gases, whereas the protein in part (a) were modeled using the density of states information.

As done in class,

$$K_C(T) = \frac{q_{H_2O}}{q_{H_2}\left(q_{O_2}\right)^{1/2}} = \frac{\left(q_t q_r q_v q_e\right)_{H_2O}}{\left(q_t q_r q_v q_e\right)_{H_2}\left(q_t q_r q_v q_e\right)_{O_2}^{1/2}} = K_t K_r K_v K_e$$

$$\ln K_C(T) = \ln K_t + \ln K_r + \ln K_v + \ln K_e$$

(5)

Now, we will examine the temperature dependence of each of the K_i's in order to determine the temperature dependence of Eq. (5).

Using the ideal gas models that we derived in class and abstracting the temperature dependence yields,

$$K_e = f\left(\frac{e^{1/T}}{e^{1/T}e^{1/T}}\right) = f\left(e^{1/T}\right) \text{ where } f \text{ is some function.}$$

$$\ln K_e = f\left(\frac{1}{T}\right)$$

(6)

The electronic part of the equilibrium constant follows van't Hoff behavior.

Examining the temperature dependence of the rotational part,

$$K_r = g\left(\frac{T^{3/2}}{TT^{1/2}}\right) = g\left(T^0\right)$$

(7)

So, the rotational part of the equilibrium constant is not a function of temperature.

$$K_t = h\left(\frac{T^{3/2}}{T^{3/2}T^{3/4}}\right) = h\left(T^{-3/4}\right)$$

$$\ln K_t = \ln\left[h\left(T^{-3/4}\right)\right]$$

(8)

Although the translational portion does not follow van't Hoff behavior, as long as it is small, which it should be, the equilibrium constant will van't Hoff behavior.

The vibrational part of the equilibrium constant is the most complicated one to analyze.

$$K_v = \left(\frac{\prod_{i=1}^{3}\left(e^{-\theta_{v_i,H_2O}/2T}\right)}{\left(e^{-\theta_{v,H_2}/2T}\right)\left(e^{-\theta_{v,O_2}/4T}\right)} \right) \left(\frac{\left(1-e^{-\theta_{v,H_2}/T}\right)\left(1-e^{-\theta_{v,O_2}/T}\right)^{1/2}}{\left(1-e^{-\theta_{v,H_2O}/T}\right)} \right) \tag{9}$$

The first set of terms in Eq. (9) all have $e^{1/T}$ dependence, so they will follow van't Hoff behavior.

However, the remaining terms require further investigation. Taking the natural log of these terms and noting that $\theta_i \gg T$ means that $e^{-\theta i/T}$ will be small. We can expand the natural log of these terms in a Taylor series and truncate after the second term.

$$\ln\left(1-e^{-\theta_i/T}\right) \approx 1-e^{-\theta_i/T}-1 = -e^{-\theta_i/T} \tag{10}$$

Applying Eq. (10) to (9)

$$\ln K_v = -e^{-\theta_{v,H_2}/T} - \tfrac{1}{2}e^{-\theta_{v,O_2}/T} + \sum_{i=1}^{3}e^{-\theta_{v,H_2O}/T} \tag{11}$$

If the θ_i's are similar, then Eq. (11) reduces to,

$$\ln K_v \approx \tfrac{3}{2}e^{-\theta_i/T} \tag{12}$$

Since $e^{-\theta i/T}$ will be small, the contribution of $\ln K_v$ to the equilibrium constant will be small. Thus, the deviation from van't Hoff behavior of the equilibrium constant due to the vibrational part will be negligible.

Plugging Eqs. (6), (7), (8), and (12) into (5) yields,

$$\ln K_C(T) = \ln\left[h\left(T^{-3/4}\right)\right] + \ln g\left(T^0\right) + \tfrac{3}{2}e^{-\theta_i/T} + f\left(\frac{1}{T}\right) \tag{13}$$

The translational and vibrational portions of the equilibrium constant have very different temperature dependencies. As long as both of these terms are small and/or cancel each other out, the equilibrium constant will follow van't Hoff behavior.