University of Washington
Department of Chemistry
Chemistry 452
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Lecture 9 7/14/14

A. Third Law of Thermodynamics

The equation of Boltzmann states that the absolute entropy S can be related to the number of microstates in the macroscopic state W. $S = k_B \ln W$. W is sometimes called the degeneracy of the system. In thermodynamic processes, only changes in state function ΔU, ΔH, ΔS, etc. are calculated, but the equation of Boltzmann provides a means to obtain absolute entropies experimentally. The means to do this is summarized as the Third Law of Thermodynamics:

- *The entropy of any pure substance (element or compound) in its equilibrium state approaches zero at an absolute temperature of zero (i.e. T=0K).*

- The basic explanation of this Law is given by the equation Temperature specifies the distribution of particles among the quantum mechanical states of a system. As the temperature increases more states become populated. But as the temperature approaches absolute zero i.e. $T \to 0K$, the number of populated states approaches decreases toward 1, i.e. $W \to 1$. At T=0K, where W=1, the absolute entropy $S=k_B ln(1)=S_0=0$.

- The standard, absolute entropy at P=1 atm. and at a temperature T $S^0(T)$ can be measured by beginning at T=0K where the absolute entropy $S^0(0)=0$ and calculating the increase of entropy with temperature using the expression

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{P,m}(solid)}{T} dT \qquad (9.1)$$

- and when a phase transition is passed adding the entropy increase

$$\Delta S = n\frac{\Delta H}{T} \qquad (9.2)$$

where is the molar heat of the phase transition, and T is the temperature of the phase transition. In general :

$$S_m^0 = \frac{S^0(T)}{n} = \int_0^{T_{fusion}} \frac{C_{P,m}(solid)}{T} dT + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{T_{fusion}}^{T_{fvap}} \frac{C_{P,m}(liquid)}{T} dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_{P,m}(vapor)}{T} dT$$

(9.3)

<u>Example 1</u>: Calculate entropy changes under standard conditions (P=1atm, T=298.15K) for the reaction $\frac{1}{2}N_2(g) + O_2(g) \rightleftarrows NO_2$

Using the data found in appendix 1 of the ERD text to calculate the entropy change of the system, surroundings, and the entropy change for the universe. Is the direction of the reaction as shown the spontaneous direction for the reaction at T=298K,

a) Entropy of system

$$S^0\left(N_2(g)\right) = 191.50 J / mole \cdot K$$

$$S^0\left(O_2(g)\right) = 205.03 J / mole \cdot K$$

$$S^0\left(NO_2(g)\right) = 239.95 J / mole \cdot K$$

$$\Delta S^0 = S^0\left(NO_2(g)\right) - S^0\left(O_2(g)\right) - \tfrac{1}{2} S^0\left(N_2(g)\right)$$

$$= (1mol)(239.95 J / mole \cdot K) - (1mol)(205.03 J / mole \cdot K) - 0.5mol \times 191.50 J / mole \cdot K = -58.83 JK^{-1}$$

b) Entropy of surroundings. This can be calculated by assuming the heat of the reaction is exchanged with the surroundings at T=298K. The heat of the reaction can be calculated from standard enthalpies of formation...also found in appendices in our text and other texts...

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T_{surr}} = -\frac{\Delta H_{sys}}{T_{surr}} = -\frac{\Delta H_f^0}{T_{surr}} = -\frac{33200J}{298K} = -111 JK^{-1}$$

c) The entropy change of the universe is obtained by summing the results from parts a and b…

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr} = (-111. - 58.83) JK^{-1} = -170. JK^{-1}$$

The negative entropy change for the universe indicates that the direction written for the reaction is not the spontaneous direction at T=298K.

<u>Example 2</u> Repeat the entropy change calculation in example 1, but do so at T=400K.

	$\Delta H^\circ_{f,291K}$ (kJ mol^{-1})	$C_{P,m}(T)\left(JK^{-1}mol^{-1}\right)$
$NO_2(g)$	33.2	$32.06 - 9.84\times10^{-3}\frac{T}{K} + 1.3807\times10^{-4}\frac{T^2}{K^2} - 1.8157\times10^{-7}\frac{T^3}{K^3}$
$N_2(g)$	0	$30.81 - 11.87\times10^{-3}\frac{T}{K} + 2.3968\times10^{-5}\frac{T^2}{K^2} - 1.0176\times10^{-8}\frac{T^3}{K^3}$
$O_2(g)$	0	$32.83 - 36.33\times10^{-3}\frac{T}{K} + 1.1532\times10^{-4}\frac{T^2}{K^2} - 1.2194\times10^{-7}\frac{T^3}{K^3}$

Solution: The most efficient way to do this problem is to calculate $\Delta C_P^0(T)$ for the temperature dependent heat capacities provided. I recommend doing things this way because you only have to do a single integral for each state function. In the table below I calculate $\Delta C_P^0(T)$...

	$C_{P,m}(T)\left(JK^{-1}mol^{-1}\right)$
$NO_2(g)$	$32.06-9.84\times10^{-3}\frac{T}{K}+1.3807\times10^{-4}\frac{T^2}{K^2}-1.8157\times10^{-7}\frac{T^3}{K^3}$
$N_2(g)$	$30.81-11.87\times10^{-3}\frac{T}{K}+2.3968\times10^{-5}\frac{T^2}{K^2}-1.0176\times10^{-8}\frac{T^3}{K^3}$
$O_2(g)$	$32.83-36.33\times10^{-3}\frac{T}{K}+1.1532\times10^{-4}\frac{T^2}{K^2}-1.2194\times10^{-7}\frac{T^3}{K^3}$
$\Delta C_P = C_P(NO_2)-\frac{1}{2}C_P(N_2)-C_P(O_2)$	$-16.175+32.425\times10^{-3}\frac{T}{K}-0.9709\times10^{-4}\frac{T^2}{K^2}-0.0875\times10^{-7}\frac{T^3}{K^3}$

Then the enthalpy calculation goes like:

$$\Delta H_{reac}(400K)=\Delta H_{reac}(298K)+\int_{298K}^{400K}\Delta C_P^0(T)dT$$

$$=\Delta H_{reac}(298K)+\int_{298K}^{400K}\left(-16.175+32.425\times10^{-3}\frac{T}{K}-0.9709\times10^{-4}\frac{T^2}{K^2}-0.0875\times10^{-7}\frac{T^3}{K^3}\right)dT$$

$$=\Delta H_{reac}(298K)-16.175T+32.425\times10^{-3}\frac{T^2}{2}-0.9709\times10^{-4}\frac{T^3}{3}-0.0875\times10^{-7}\frac{T^4}{4}\Bigg|_{298}^{400}$$

$$=33200J-(16.175J)(400-298)+\left(32.425\times10^{-3}\right)\left(\frac{400^2-298^2}{2}\right)$$

$$-0.9709\times10^{-4}\left(\frac{400^3-298^3}{3}\right)-0.0875\times10^{-7}\left(\frac{400^4-298^4}{4}\right)$$

$$=33200J-(16.175J)(102)+\left(32.425\times10^{-3}J\right)(35598)$$

$$-0.9709\times10^{-4}J\left(1.251\times10^7\right)-0.0875\times10^{-7}J\left(4.428\times10^9\right)$$

$$\therefore\ \Delta H_{reac}(400K)=33200J-1650J+1154J-1215J-38.75J=31450J$$

The entropy calculation goes like:

$$\Delta S_{reac}\left(400K\right)=\Delta S_{reac}\left(298K\right)+\int_{298K}^{400K}\frac{\Delta C_P^0\left(T\right)}{T}dT$$

$$=\Delta S_{reac}\left(298K\right)+\int_{298K}^{400K}\left(\frac{-16.175}{T/K}+32.425\times10^{-3}-0.9709\times10^{-4}\frac{T}{K}-0.0875\times10^{-7}\frac{T^2}{K^2}\right)dT$$

$$=\Delta S_{reac}\left(298K\right)-16.175\ln\left(\frac{400}{298}\right)+32.425\times10^{-3}\left(400-298\right)$$

$$-0.9709\times10^{-4}\left(\frac{400^2-298^2}{2}\right)-0.0875\times10^{-7}\left(\frac{400^3-298^3}{3}\right)$$

$$=-58.83JK^{-1}-4.76JK^{-1}+3.31JK^{-1}-3.46JK^{-1}-0.110JK^{-1}=-63.85JK^{-1}$$

$$\therefore\Delta S_{sys}=\Delta S_{reac}\left(400K\right)=-63.85JK^{-1}$$

$$\Delta S_{surr}=\frac{\Delta H_{surr}}{T_{surr}}=-\frac{\Delta H_{sys}}{T_{surr}}=-\frac{31450J}{400K}=-78.63JK^{-1}$$

$$\Delta S_{universe}=\Delta S_{sys}+\Delta S_{surr}=-63.85JK^{-1}-78.63JK^{-1}=-142.5JK^{-1}$$

The entropy change at T=400K still does not favor this reaction in the direction indicated.