CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

. Physical Chemistry, Robert J. Silbey, Robert A. Alberty, Moungi G. Bawendi

. Physical Chemistry, Ira N. Levine

The Second and Third Laws

Entropy change of surroundings:

$$dS_{sur} = \frac{dq_{sur}}{T_{sur}} \rightarrow \Delta S_{sur} = \frac{q_{sur}}{T_{sur}}$$

For any adiabatic change q_{sur} =0 so $\Delta S_{sur} = 0$ adiabatic change

The statistical definition of entropy

$S = klnW$ Boltzman formula for the entropy

k: Boltzman's constant (k=1.381*10^{-23} J/K)

W: the number of microstates: the molecules of a system can be distributed over the energy states for a specified total energy.

$$\oint dS = \oint \frac{dq_{rev}}{T} = 0$$

$\oint$ denotes integration around in a closed path

The Second and Third Laws

Carnot Cycle: consists of four reversible stages

Stage 1: $q_h = nRT_h ln\frac{V_A}{V_B}$

Stage 3: $q_c = nRT_c ln\frac{V_D}{V_C}$

Stage 4: $V_A T_h^c = V_D T_c^c$

Stage 2: $V_C T_c^c = V_B T_h^c$

$$V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c \qquad \frac{V_D}{V_C} = \frac{V_A}{V_C}$$

The total change in entropy around the cycle is the sum of the changes in each of these four steps.

The Second and Third Laws

The total change in entropy around the cycle is the sum of the changes in each of these four steps.

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c} \quad q_c = nRT_c ln\frac{V_D}{V_C} = nRT_c ln\frac{V_A}{V_B} = -nRT_c ln\frac{V_B}{V_A} \qquad \frac{q_h}{q_c} = \frac{nRT_h ln\frac{V_A}{V_B}}{-nRT_c ln\frac{V_B}{V_A}} = \frac{T_h}{T_c}$$

$$\frac{q_h}{T_h} + \frac{q_c}{T_c} = 0$$

Efficiency

$$\eta = \frac{work\ performed}{heat\ absorbed\ from\ hot\ source} = \frac{|w|}{|q_h|} = \frac{|q_h| - |q_c|}{|q_h|} = 1 - \frac{|q_c|}{|q_h|}$$

$\boldsymbol{\eta = 1 - \frac{T_c}{T_h}}$ Carnot efficiency

The Second and Third Laws

Entropy changes accompanying specific processes

The change in entropy of a perfect gas that expands isothermally from V_i to V_f is

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

The total change in entropy, however, does depend on how the expansion takes place.

$$\Delta S_{sur} = \frac{q_{sur}}{T} = -\frac{q_{rev}}{T} = -nR\ln\frac{V_f}{V_i}$$

The total entropy change is given

$$\Delta S_{tot} = nR\ln\frac{V_f}{V_i}$$

Entropy of phase transitions: $\Delta_{trs}S(\Delta S_{trs}) = \frac{q}{T_{trs}} = \frac{\Delta_{trs}H}{T_{trs}}$

The Second and Third Laws

Entropy changes accompanying specific processes

Heating:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

When Cp is independent of temperature over temperature range of interest

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_p ln \frac{T_f}{T_i}$$