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

THERMOCHEMISTRY

Adiabatic changes:

Provided the capacity is independent of temperature, the change in the internal energy is

$$\Delta U = (T_f - T_i)C_v = C_v\Delta T$$

Because the expansion is adiabatic $q = 0$, $\Delta U = q + w \rightarrow \Delta U = w_{adiabatic} = C_v\Delta T$ (work of adiabatic change)

In a reversible adiabatic expansion: For a perfect gas

$\Delta U = C_v\Delta T,\ C_v dT = -pdV = -\frac{nRT}{V}$dV

$$C_v\frac{dT}{T} = -nR\frac{dV}{V}\ integration\ \ C_v\int_{T_i}^{T_f}\frac{dT}{T} = -nR\int_{V_i}^{V_f}\frac{dV}{V} \rightarrow C_v ln\frac{T_f}{T_i} = -nRln\frac{V_f}{V_i}$$

THERMOCHEMISTRY

Adiabatic changes:

$$\frac{C_v}{nR} ln\frac{T_f}{T_i} = ln\frac{V_f}{V_i} \rightarrow \frac{C_v}{nR} = \frac{C_{v,m}}{R} = c$$ (and use $lnx^a = alnx$)

$$ln\left(\frac{T_f}{T_i}\right)^c = ln\frac{V_f}{V_i} \Rightarrow T_f = T_i\left(\frac{V_f}{V_i}\right)^c$$

$$V_i T_i^c = V_f T_f^c$$

note: $\frac{C_{v,m}}{R} = c$ (temperature change reversible adiabatic expansion, perfect gas)

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

THERMOCHEMISTRY

Adiabatic changes:

The change in pressure:

$$\frac{P_i V_i}{P_f V_f} = \frac{T_i}{T_f} \Rightarrow \frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{1/c} \quad \text{so} \quad \frac{P_i}{P_f}\left(\frac{V_i}{V_f}\right)^{(1/c)+1} = 1$$

$C_{p,m} - C_{v,m} = R$ (perfect gas)

$$\frac{1}{c} + c = \frac{1+c}{c} = \frac{\overbrace{R + C_{v,m}}^{C_{p,m}}}{C_{v,m}} = \frac{C_{p,m}}{C_{v,m}} = \gamma$$ Therefore $$\frac{P_i}{P_f}\left(\frac{V_i}{V_f}\right)^{\gamma} = 1$$ which rearranges to

$$p_i V_i^{\gamma} = p_f V_f^{\gamma}$$ pressure change reversible adiabatic expansion, perfect gas

For a monoatomic gas, perfect gas $C_{v,m} = \frac{3}{2}R \Rightarrow C_{p,m} = \frac{5}{2}R$ $C_{p,m} - C_{v,m} = R$ so $\gamma = \frac{5}{2}$

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

The Second and Third Laws

Entropy: It shows disorder and efficiency of a system

Entropy change expressed

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

dq_{rev}: energy transferred as heat reversibly to the system at the absolute temperature.

For a measurable change between two states i and f , extensive property

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} \left(\frac{Joule}{Kelvin}\right)$$

Molar entropy, intensive property

$$S_m = \frac{S}{n} \left(\frac{J}{molK}\right)$$

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