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 formulation of the First Law:

Heat and work are equivalent ways of changing the internal energy of system. The internal energy of an isolated system is constant (The First Law of thermodynamics).

$\Delta U = q + w$ (Mathematical statement of the First Law)

Expansion work:

$dU = dq + dw,\ \ dw = -|F|dz\ \ (work\ done)$ (-) sign implies internal energy decreasing.

$$w = -\int_{V_i}^{V_f} p_{ex} dV$$

Expansion against constant pressure:

$$w = -p_{ex}\int_{V_i}^{V_f} dV = -p_{ex}\left(V_f - V_i\right) = -p_{ex}\Delta V$$

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The formulation of the First Law:

Reversible expansion: a change that can be reversed;

$$dw = -p_{ex}dV = -pdV$$

p_{ex}: external pressure of gas

p: pressure of gas (in the vessel)

$$w = -\int_{V_i}^{V_f} pdV \rightarrow p = \frac{nRT}{V} \rightarrow w = -nRT\int_{V_i}^{V_f} \frac{dV}{V} = -nRT ln\left(\frac{V_f}{V_i}\right)$$

work of reversible expansion (perfect gas).

Heat transactions:

In general, the change in internal energy;

$$dU = dq + dw_{exp} + dw_{add}$$

At constant V, dw_{exp}=0, however if there is no addition work

$dU = dq$ Heat transferred at constant volume or $dU = dq_V$

$\int_i^f dU = \int_i^f dq_V \rightarrow \Delta U = q_V$ q_v is not written as Δq_v, because q is not a state function.

Heat capacity

$C_V = \left(\frac{\partial U}{\partial T}\right)_V$ Heat capacity at constant volume

$$dU = C_V dT = C_V \int_i^f dT = C_V(T_f - T_i) \rightarrow \Delta U = C_V \Delta T$$

$$q_V = C_V \Delta T$$

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Enthalpy

$H = U + PV$ definition

For a general infinitesimal always change in the state of the system. Changes;

U→U+dU

p→p+dp

V→V+dV

$$dH = dU + pdV + Vdp$$

$$dU = dq + dw$$

$$dH = dq + dw + pdV + Vdp \rightarrow dH = dq + Vdp$$

at constant p $dH = dq_p$

$\Delta H = \Delta U + \Delta nRT$ relation between ΔH and ΔU

Enthalpy

$C_p = \left(\frac{\partial H}{\partial T}\right)_p$ Heat capacity at constant pressure

$dH = C_p dT = C_p \int_i^f dT = C_p(T_f - T_i) \rightarrow \Delta H = C_p \Delta T$

$q_p = C_p \Delta T$

$C_{p,m} = a + bT + \frac{c}{T^2}$ a, b and c independent of temperature

$C_p - C_V = nR$

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