

Thermodynamics!



internal energy

$$\Delta U = q + w$$



$$w = -P\Delta V = -\Delta nRT$$

at constant P

$$\Delta U = q_p - P\Delta V$$

$$\Delta U = \Delta H - P\Delta V$$

$$\Delta U = \Delta H - \Delta nRT$$

FIRST LAW

Energy cannot be created or destroyed only changed in its form

$$H = U + PV$$

← definition of enthalpy

CALORIMETRY

$$\Delta U = q_v \text{ (bomb calorimetry)}$$

$$\Delta H = q_p \text{ (coffee-cup calorimetry)}$$

$$q_{cal} = m_{H_2O} C_{s,H_2O} \Delta T + C_{cal} \Delta T$$

water part hardware

$$q_{sys} = -q_{cal}$$

system heat is opposite in sign from the calorimeter!

HEATING stuff up



$$q = n C_m \Delta T$$

moles molar heat capacity in J/mol·K

$$q = m C_s \Delta T$$

mass in grams specific heat capacity in J/g·K

If heating gases you need to know all the different C_v 's & C_p 's

different types of ideal gases

C_v	C_p
monatomic $\frac{3}{2}R$	$\frac{5}{2}R$
linear $\frac{5}{2}R$	$\frac{7}{2}R$
non-linear $\frac{6}{2}R$	$\frac{7}{2}R$

2nd LAW

all spontaneous changes are accompanied by an increase in universal entropy

$$S = k \ln W$$

Boltzmann constant $k = R/N_A$
microstates

FREE ENERGY

$$G = H - TS$$

at constant P + T

$$\Delta G = \Delta H - T\Delta S$$

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

$$\Delta S = \frac{q_{rev}}{T}$$

for temp. changing

$$\Delta S = n C_p \ln \frac{T_2}{T_1}$$

* or C_v

$$\Delta G = -T\Delta S_{universe}$$

governs 2nd Law

conditional!

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S$$

$$T = \Delta H / \Delta S$$

Phase changes

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

ISOTHERMAL expansion

$\Delta T = 0$, T is constant



$$\int dw = \int -P dV$$

$$\star w = -nRT \ln \frac{V_2}{V_1}$$

$$\star q = nRT \ln \frac{V_2}{V_1}$$

$$\star \Delta S = nR \ln \frac{V_2}{V_1}$$

$$\Delta U = 0 \text{ and } \Delta H = 0 \quad q = -w$$

and! $P_1/P_2 = V_2/V_1$ (Boyle's Law)

3rd LAW

The entropy of a perfectly crystalline substance at absolute zero is zero.

When $\Delta S_{univ} = 0$

for a process, you have reached

EQUILIBRIUM!

We PREFER

$$\Delta G = 0$$

for defining equilibrium

so at equilibrium

$$\Delta G = 0 = \Delta H - T\Delta S$$

HESS' LAW

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

$$\Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{prod}) - \sum \Delta H_f^\circ(\text{react})$$

$$\Delta H_{rxn} = \sum \text{B.E.}(\text{react}) - \sum \text{B.E.}(\text{prod})$$

Bond Energies

$$\Delta G_{rxn}^\circ = \sum \Delta G_f^\circ(\text{prod}) - \sum \Delta G_f^\circ(\text{react})$$

$$\Delta S_{rxn}^\circ = \sum S^\circ(\text{prod}) - \sum S^\circ(\text{react})$$