

VC210 FALL2018 RECITATION CLASS

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November 13, 2018

Sign Convention

$$W/Q \quad \left\{ \begin{array}{ll} > 0 : & \text{energy import (endothermic for Q)} \\ < 0 : & \text{energy export (exothermic for Q)} \end{array} \right.$$

Work

Non-expansion Work

$$\Delta G = W_{\text{nonmax}}$$

Expansion Work

(a) Free expansion($p_{\text{ext}}=0$):

$$W = 0$$

(b) Constant external pressure:

$$W = -p_{\text{ext}}\Delta V$$

(c) Reversible process:

$$W = -nRT \ln \frac{V_2}{V_1}$$

Heat

Heat transfer is the result of temperature difference!

$$q = C\Delta T$$

Heat Capacity

Specific Heat Capacity

$$C_s = \frac{C}{m}$$

Molar Heat Capacity

$$C_m = \frac{C}{n} \quad \left\{ \begin{array}{l} C_{V.m.} = \frac{\Delta U}{n\Delta T} \\ C_{p.m.} = \frac{\Delta H}{n\Delta T} \end{array} \right.$$

Heat

For (ideal) gas:

$$C_{p.m.} = C_{V.m.} + R$$

	Atomic	Linear	Nonlinear
$C_{V.m.}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{p.m.}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

Laws of Thermodynamics

1st Law of Thermodynamics

The internal energy of any isolated system is constant.

$$\Delta U = W + q$$

For ideal gas: $\Delta U(\text{const } T) = 0$

2nd Law of Thermodynamics

The entropy an isolated system increases on the course of any spontaneous change, i.e. in an isolated system, $\Delta S \geq 0$.

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{surr}} = \Delta S - \frac{\Delta H}{T} \quad \left\{ \begin{array}{l} > 0 \text{ spontaneous} \\ = 0 \text{ equilibrium} \\ < 0 \text{ non-spontaneous} \end{array} \right.$$

Internal Energy U

Equipartition Theorem

Every quadratic contribution to the kinetic energy of all types of molecular motions equals to $1/2kT$.

$$k = 1.3811 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} = \frac{R}{N_A}$$

$$U_m = \begin{cases} \text{translational motion: } \frac{3}{2}RT \\ \text{rotational motion(linear): } RT \\ \text{rotational motion(nonlinear): } \frac{3}{2}RT \end{cases}$$

Entropy S

Calculations of Entropy

(a)

$$\Delta S = \frac{q_{rev}}{T} \Rightarrow \begin{cases} \text{positional disorder (const } T) & \Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{p_2}{p_1} \\ \text{thermal disorder} & \begin{cases} (\text{const } p) & \Delta S = C_{p.m.} \ln \frac{T_2}{T_1} \\ (\text{const } V) & \Delta S = C_{v.m.} \ln \frac{T_2}{T_1} \end{cases} \end{cases}$$

If more than 1 variable change, construct a path with only one constant variable.

Phase change

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \quad \Delta S_{fus} = \frac{\Delta H_{fus}}{T_f}$$

Hold only at transformation points (T_b/T_f). Other $T \rightarrow$ Born-Harber.

Entropy S

(b) Standard molar entropy ΔS_m°

$$\Delta S_m^\circ = \sum \mu S_m^\circ(\text{product}) - \sum \mu S_m^\circ(\text{reactant})$$

(c)

$$\Delta S = k \ln W$$

(d)

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

Enthalpy H

$$H = U + pV$$

Note that p here (as well as p in the ideal gas law $pV=nRT$) is the pressure of the system but p in work calculation is the external pressure (p_{ext}). For chemical reactions which are often conducted in an open system, the external pressure equals the internal pressure. (Review Exercise, part II, 12)

Gibbs Free Energy G

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ (constant } T\text{)}$$

ΔG is the maximum amount of non-expansion work that can be done by the system.

$$\Delta G = W_{non,max}$$

(a)

$$\text{Spontaneity} \begin{cases} \Delta G < 0 \text{ spontaneous} \\ \Delta G = 0 \text{ equilibrium} \\ \Delta G > 0 \text{ non-spontaneous/reverse spontaneous} \end{cases}$$

Gibbs Free Energy G

(b) Gibbs Free Energy of Reaction

$$\Delta G = \sum nG_m(\text{product}) - \sum nG_m(\text{reactant})$$

ΔG is not constant throughout the reaction! It is not in the standard condition. ΔG depends on the amount of substance.

(c) Standard Gibbs Free Energy of Reaction

$$\Delta G^\circ = \sum nG_m^\circ(\text{product}) - \sum nG_m^\circ(\text{reactant})$$

ΔG° is constant because it is defined under standard condition. The amount of matter is determined (1bar/1mol/L)

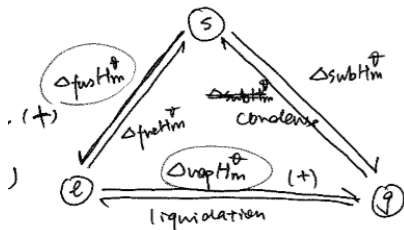
(d) Standard Gibbs Free Energy of Formation

$$\Delta G_f^\circ \begin{cases} > 0 \text{ thermodynamically stable} \\ < 0 \text{ thermodynamically unstable} \end{cases}$$

Physical Change

Phase Change

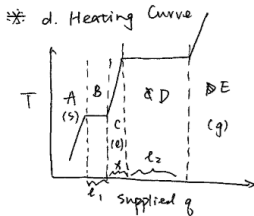
Phase change under **transformation points** are all reversible process



$\Delta_{fus}H_m^\circ$ and $\Delta_{vap}H_m^\circ$ are enough to deduce the other physical change enthalpy.

Physical Change

Heating Diagram



- ① A, C, E are pure matter
B, D are transient states

- ② The steeper the slope of a heating curve,
the lower is the heat capacity.
(For H₂O, $k_c < k_A$, $k_c < k_E$)

- ③ B - melting point, D - boiling point. T is constant
at transient points.

④ $l_1 = n \Delta_{\text{fus}} H_m^\ominus$; $l_2 = n \Delta_{\text{vap}} H_m^\ominus$

$x = nC(T_2 - T_1)$

Attention

Matter states in different intervals; relationship between slope and heat capacity; boiling point & melting point; how to calculate the length of each interval.

Thermochemistry

Standard State

pure form + 1 bar(g)/1 mol/L(aq)

Note: standard state does not have temperature restrictions! Each temperature has its own standard state. However, common chemical constants are assumed to be under 298.15K if there are no specific declaration.

Stand Enthalpy of Combustion

1 mol fuel $\xrightarrow[\text{burn}]{O_2}$ most stable form

Stand Enthalpy of Formation

most stable simple substance \longrightarrow **1 mol** product

$\Delta_c H_m^\circ$ and $\Delta_f H_m^\circ$ are relevant in some situations:

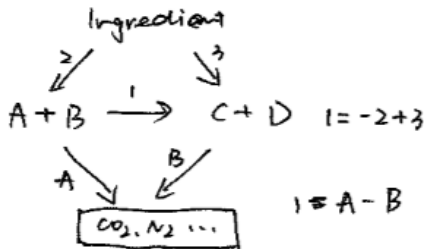
$\Delta_c H_m^\circ(\text{graphite}) = \Delta_f H_m^\circ(CO_2)$. They describe the same reaction.

Thermochemistry

Application of $\Delta_c H_m^\circ$ and $\Delta_f H_m^\circ$

$$\begin{aligned}\Delta_r H_m^\circ &= \sum \mu \Delta_f H_m^\circ(\text{product}) - \sum \mu \Delta_f H_m^\circ(\text{reactant}) \\ &= \sum \mu \Delta_c H_m^\circ(\text{reactant}) - \sum \mu \Delta_c H_m^\circ(\text{product})\end{aligned}$$

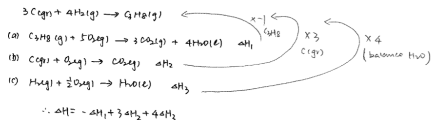
(vector relationship)



Thermochemistry

Hess's Law

ΔH can be added or multiplied by some number following the reaction.



Kirchhoff's Law

$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \Delta C_p(T_2 - T_1)$$

$$C_p = \sum n C_{p.m.}(\text{product}) - \sum n C_{p.m.}(\text{reactant})$$

Born-Harber Cycle

Suggestions!

Be careful with calculations!

Use Hess's Law if you are not confident in ΔH_c and ΔH_f !

Remember the states(g/l/s) of each substance in Born-Harber cycle!

Thank you !