

CHIEMI465-665 Thermodynamics



Final summary

Thermodynamics Relationship between macroscopic properties of a system.

Kinetics

Chemical kinetics, is the study of rates of chemical processes.

Quantum mechanics

Quantummechanicsdealswithphenomenaandobjectsofnanoscopicsize.Inprinciple,quantummechanicsprovidesamathematicaldescriptionofeverything.



Simple terms







The definition of temperature

temperature definition

Two systems in thermal equilibrium with each other have the same temperature.

0th law of thermodynamics

Two systems that are found to be in thermal equilibrium with a third system will be found in thermal equilibrium.

Extensive / Intensive







Volume



Joseph Louis Gay-Lussac (1778 – 1850)



Jacques Alexandre César Charles (1746 – 1823)









P: pressureV: Volumen: particle numberT: temperature in Kelvin



Q

Heat, symbolized by Q, is energy transferred from one body or system to another due to a difference in temperature.

http://en.wikipedia.org/wiki/Heat

U In thermodynamics, the internal energy of a thermodynamic system, or a body with well-defined boundaries, denoted by U, or sometimes E, is the total of the kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules or crystals. It includes the energy in all the chemical bonds, and the energy of the free, conduction electrons in metals.

http://en.wikipedia.org/wiki/Internal_energy

Work done by the system on the surroundings	-	Gas expansion of a system against an external pressure. Snow machine (as an adiabatic process). ∆U<0, w<0
Work done on the system by the surroundings	+	Gas compression of a system by the surroundings. Inflating the tiers of a car as an adiabatic process. Δ U>0, w>0
Heat adsorbed by the system from the surroundings	+	
Heat adsorbed by the surroundings from the system	-	





 $W_{irriversible} < W_{reversible}$

Work depends on the way we choose.

A reversible process is one where the system is infinitesimally close to equilibrium.

 \rightarrow We obtain the maximum of work.



Summary – pressure work

irreversible

reversible





 $W_{irriversible} < W_{reversible}$

$$w_{rev} = -\int_{V_1}^{V_2} P_{ext} dV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} =$$
$$= -nRT \ln(V) |_{V_1}^{V_2} = -nRT [\ln(V_2) - \ln(V_1)] = -nRT \ln(\frac{V_2}{V_1})$$

0th law

Two systems, that are found to be in thermal equilibrium with a third system, will be found in thermal equilibrium.

1st law

Conservation of energy. $\Delta U = q - w$

The increase in the internal energy of a system is equal to the amount of energy added by heating the system, minus the amount lost as a result of the work done by the system on its surroundings.

How to measure heat capacities?





Constant pressure calorimeter $C_p\Delta T=q_p=\Delta H$

external pressure



gas expansions



P: pressure, V: volume, T: temperature, U: internal energy, q: heat: w:work, c_v: heat capacit

Expansion and compression









Entropy definition

Thermodynamics definition

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

The entropy change of a system in a reversible process equals the heat adsorbed divided by the temperature at which the process occurs.

S is a state function but heat not. Thus, the path must be specified in the definition of the entropy.

Statistical definition

$$\Delta S_{1->2} = k_B \ln(\frac{W_2}{W_1})$$

The entropy change of a system is given by the probability ratio of the final and initial states. The entropy of an isolated system increases in an irreversible process and remains unchanged in a reversible process. The total entropy can never decrease. $\Delta S = \Delta S_{sys} + \Delta S_{surr} = \begin{cases} 0 \text{ for reversible} \\ > 0 \text{ for irreversible} \end{cases} \text{process}$

A system develops towards the state with the greatest probability.

Short version of the laws

0 th law	Definition of the temperature considering the equilibrium of systems.
1 st law	$\Delta U = q + w$
2 nd law	$\Delta S = \Delta S_{sys} + \Delta S_{surr} = \begin{cases} 0 \text{ for reversible} \\ > 0 \text{ for irreversible} \end{cases} \text{ process}$
3rd law	$\lim_{T\to 0K} \Delta S = 0$

Some properties of the entropy (S)

→ S is a state function (S does not depend on the path chosen: initial → final state) → S is extensive $(S_{tot} = S_1 + S_2 + ...)$ → $\Delta_{vap}S > 0$ and $\Delta_{fus}S > 0$

 \rightarrow S_{gas} > S_{liquid} > S_{solid} (per mole)

→ S ~ size of a molecule (Why?:# of degrees of freedom increase with number of atoms)

→ P→0 then S → ∞ (Why? $\Delta S = nRln(V_2/V_1)$ V₁: reference volume V₂ → ∞ for P → 0)

⇒ S ≥ 0 (Why: T = 0K → w = 1 (perfect crystal) ⇒ S = k_B ln(w) = 0, note that w > 1 and S increases with temperature) ⇒ S increases with temperature $\Delta S_T^{\circ} = \Delta S_{298.15}^{\circ} + \int_{298.15}^{T} \frac{\Delta C_P^{\circ}}{T'} dT' \quad \text{Eq.}(5.43)\text{-Engel}$ $\Rightarrow S_{\text{diamond}} < S_{\text{graphite}} \quad (Why?: High degree of order reduced S)$ Some properties of the entropy (S)

 \rightarrow S is a state function (S does not depend on the path chosen: initial \rightarrow final state)

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⇒ P→0 then S → ∞ (Why?
$$\Delta S = nRln(V_2/V_1)$$

V₁: reference volume
V₂ → ∞ for P → 0)

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→ S =
$$k_B \ln(w) = 0$$
, w > 1)

 \rightarrow S increases with temperature

$$\Delta S_T^{\circ} = \Delta S_{298.15}^{\circ} + \int_{298.15}^T \frac{\Delta C_P^{\circ}}{T'} dT' \quad \text{Eq.(5.43)-Enge}$$



 \rightarrow S_{diamond} < S_{graphite} (Why?: High degree of order reduced S)

Some properties of the entropy (S)

 \rightarrow S_{diamond} < S_{graphite} (Why?: High degree of order reduced S)

→ More complex systems have larger S ($S_{ozone} > S_{O2}$)

→ S increases with the volume of a gas (Why?: $\Delta S \sim \ln(V_2/V_1)$)

 $S(N_2 @ 0.1 atm) > S(N_2 @ 1 atm)$





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 \rightarrow Entropy change of a reaction $aA + bB + ... \rightarrow cC + dD + ...$

aA + bB + ... → cC + dD + ... $\Delta_r S = \sum v S(\text{products}) - \sum n S(\text{reactants})$

$$\Delta S_R^\circ = \sum_i v_i S_i^\circ \quad \text{Eq.(5.41)}$$

Gibbs energy

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 $\Delta G < 0$ for spontaneous process

Basic Equations



 $dH = dq_P$ (P = const)

Gibbs energy

G = H-TS

for P and T = const dG = dH - TdS $0 \ge dG$ $\Delta G = w_{max}$ $dU = dq_V$ (V = const)

Helmholtz energy

 $\mathbf{A} = \mathbf{U} \mathbf{-} \mathbf{T} \mathbf{S}$

for V and T = const dA = dU - TdS $0 \ge dA$ $\Delta A = w_{max}$



Follows from 2nd law of thermodynamics



-TS: heat TAX

Discuss this equation. What is the meaning of the TS term? What actually is work? Why is A smaller than U? A = U – TS ??

Perhaps like that:

- Work in the most basic sense is energy transfer by the uniform motion of atoms. Therefore, work done on the surroundings is energy transferred to the surroundings as the uniform motion of atoms. (using some kind od device to do so.)
- **Opposed to entropy (or TS=q)**

which is energy stored in a disordered way and therefore cannot directly be used to perform work.

→ Therefore, only the contribution to the internal energy that is not stored in a disordered manner can be transferred into work (that is U-TS).

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Phase equilibrium

Phase equilibrium: freezing: solid-liquid boiling: liquid – gas

crystal structures: graphite - diamond

How to define the equilibrium? What phase is stable?

Equilibrium condition:

 $\mathbf{G}_{\text{phase-1}} = \mathbf{G}_{\text{phase-2}}$

(molar Gibbs energies)

Rule: Stable phase has lower G

4.40 A certain reaction is known to have a $\Delta_r G^o$ value of -122 kJ. Will the reaction necessarily occur if the reactants are mixed together?

Reaction conditions may differ from standard conditions.

More importantly: Kinetic limitations. Mr. Gibbs predicts the equilibrium but not the "speed" for approaching it.

Typical mistakes: $\Delta G > 0 \rightarrow$ noting will happen $\Delta G < 0 \rightarrow$ the reaction will always occur

Wrong

Correct

 $\Delta G > 0$ Reverse reaction may be spontaneous $\Delta G < 0$ Kinetic limitations

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 $\Delta G < 0$ for spontaneous process

 $\mu_i^I > \mu_i^{II}$ for spontaneous mass transfer of species i from system I to II

The chemical potential appears rather abstract. Perhaps the following comparisons might help.

scenario	driving force	
flow of heat	reservoirs at different	
	temperatures i.e.	
	$\Delta T > 0$	
work "flows", work done on		
a system (pushing a piston)	$\Delta p > 0$	
flow of chemical species i	$\Delta \mu > 0$	
from one phase to another		

the chemical potential \rightarrow "measures the tendency of escaping particles"

State function	Equilibrium
$\Delta T \approx 0$	thermal
$\Delta p \approx 0$	mechanical
$\Delta \mu_i \approx 0$	material

$\boldsymbol{\mu}$ is called a potential because ..

of the analogy with a mechanical system:



Max \rightarrow Min

Here $\mu_{max} \rightarrow \mu_{min}$

- \bullet Stable phase/species has the lower μ
- At equilibrium $\mu_{\alpha} = \mu_{\beta}$

 2^{nd} law \rightarrow Gibbs \rightarrow Chemical potential \rightarrow Equilibrium constant

Chemical equilibrium

$$\Delta_r G^0 = -RT \ln(K_P)$$

$$\Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0$$

 $\mathbf{K}_{p} = \mathbf{K}_{p}(\mathbf{T}) - \mathbf{van't}$ Hoff equation

Differential version

$$\frac{d\ln K_P}{dT} = -\frac{1}{R} \frac{d(\Delta G_{reaction}^{\circ}/T)}{dT} = \frac{\Delta H_{reaction}^{\circ}}{RT^2}$$

Integrated version

$$\ln K_P(T_f) = \ln K_P(298.15 \text{ K}) - \frac{\Delta H_{reaction}^{\circ}}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}}\right)$$



Jacobus Henricus van 't Hoff

Indefinite integrated version

$$\ln(K_p) = -\frac{\Delta H_r^0}{R} \frac{1}{T} + \frac{\Delta S_r^0}{R}$$



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If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or total pressure, then the equilibrium shifts to partially counter-act the imposed change.



Henry Louis LeChâtelier (1850 – 1936) was a French chemist of the late 19th and early 20th centuries. He is most famous for devising Le Chatelier's principle, used by chemists to predict the effect of a change in conditions on a chemical equilibrium.







Le Chatelier's principle

Jacobus Henricus van 't Hoff

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Phase diagrams

Can you discuss these diagrams?



Phase rule

PChem – Thermodynamics class



Clausius-Clapeyron Equation



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Solutions

Vocabulary words:
$$x_i, M, m$$
Mole
fractionmolality
molarityPartial molar quantities $\overline{X} = \frac{\partial x}{\partial n_i} |_{T,P}$ X can be H, G, VPartial molar
volumePartial molar
Gibbs energy (chemical potential) $\overline{V_1} = \frac{\partial V}{\partial n_1} |_{T,P}$ $\overline{G_1} = \frac{\partial G}{\partial n_1} |_{T,P} = \mu_1$ $V = n_1 \overline{V_1} + n_2 \overline{V_2} + \dots$ $\overline{G} = n_1 \mu_1 + n_2 \mu_2 + \dots$ $\sum V_m \neq V$ $\overline{G_\alpha} = \overline{G_\beta}$
 $\mu_\alpha = \mu_\beta$

Chemical potential – multicomponent systems

 $\mu(g) = \mu_1^0 + RT \ln(P/P^0)$ gas phase, single component



Chemical potential of component I in solution = chemical potential of pure liquid * ln (pressure of solution/pure vapor pressure)

Solutions – simple laws

for solvent		
$P_1 = x_1 P_1^*$		

Rault's law

Henry's law for solute $P_2 = K m$

1: solvent 2: solute m: molality x: mole fraction K: constant



Opening a can. What happens? Pressure of solute (CO_2) , P_2 , above solution is proportional to solute molality, m.

> Reducing pressure \rightarrow reduces molality \rightarrow gas bubbles out of the solution.

> > One can also say: solubility of the gas depends (at least indirectly) on pressure. Reducing that pressure reduces solubility and the excess gas escapes.



SUMMARY - Osmotic pressure

The term osmotic pressure of a solution refers to the pressure that must be applied to the solution to increase the chemical potential of the solvent to the value of its pure liquid under atmospheric pressure.



Osmosis: solvent \rightarrow solution low $c_{solute} \rightarrow high c_{solute}$

initially

 $\mu_1^{Left} > \mu_1^{Right}$

at equilibrium
$$\begin{cases} \mu_1^L = \mu_1^R \\ \mu_1^* = \mu_1^* + RT\ln(x_1) + \Pi \overline{V} \end{cases}$$

1) Solvent

2) Solute

The process is the diffusion of fresh/clean water to from the high concentrated salty seawater into the tube with clean water.

Osmosis: pressure is generated automatically by difference in chemical potential.

Reverse osmosis: we need to generate somehow the required pressure externally.

Osmosis: solvent	$t \rightarrow solution$	
low c	→ high c	
Reverse osmosis:	solution water + salt high c	 → solvent → water → low c

