## CIHIEMI465-665

## Therrmodyymamics



Final summary

## Kinetics

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

## Quantum mechanics

Quantum mechanics deals with phenomena and objects of nanoscopic size. In principle, quantum mechanics provides a mathematical
description of close to everything.

## GQS I®WS

Sinmple rerpons

## Basic definitions


open

closed

isolated

## The definition of temperature

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

$0^{\text {th }}$ 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

Consider $\rightarrow$


V1 + V2 =
$\mathbf{M 1}+\mathbf{M} 2=$
result is equal to the sum of its values


T1 + T2 = $\delta 1+\delta 2=$
result does not depend on the amount of matter

Extensive


Properties which are directly proportional to the material present are called extensive.

Force, volume, mass
T, density, molar volume
http://en.wikipedia.org/wiki/Intensive_property


## Robert Boyle

 (1627-1691)He met Galileo Galilei



Joseph Louis Gay-Lussac (1778-1850)


Jacques Alexandre César Charles (1746-1823)





P: pressure
V: Volume
n: particle number
T : temperature in Kelvin


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

In thermodynamics, the internal energy of a thermodynamic system, or a body with welldefined boundaries, denoted by $\boldsymbol{U}$, 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 <br> surroundings | - | Gas expansion of a system against an external <br> pressure. <br> Snow machine (as an adiabatic process). $\Delta \cup<0, w<0$ |
| :--- | :--- | :--- |
| Was compression of a system by the surroundings. |  |  |
| Work done on the system by the <br> surroundings | +Inflating the tiers of a car as an adiabatic process. <br> $\Delta \cup 0, w>0$ |  |
| Heat adsorbed by the system from the <br> surroundings | $+\cdots$ |  |
| Heat adsorbed by the surroundings from <br> the system | - | $\cdots$ |


$w_{\text {irriversible }}<w_{\text {reversible }} \quad$ 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


$$
w_{r e v}=-\int_{V_{1}}^{V_{2}} P_{e x t} d V=-\int_{V_{1}}^{V_{2}} \frac{n R T}{V} d V=-n R T \int_{V_{1}}^{V_{2}} \frac{d V}{V}=
$$

$$
=-\left.n R T \ln (V)\right|_{V_{1}} ^{V_{2}}=-n R T\left[\ln \left(V_{2}\right)-\ln \left(V_{1}\right)\right]=-n R T \ln \left(\frac{V_{2}}{V_{1}}\right)
$$

> 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.

$$
\Delta \mathbf{U}=\mathbf{q}-\mathbf{w}
$$

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 volume |
| :--- |
| calorimeter |
| $\mathrm{C}_{\mathrm{V}} \Delta \mathrm{T}=\mathrm{q}_{\mathrm{V}}=\Delta \mathrm{U}$ |

gnition wire


Constant pressure calorimeter $\mathrm{C}_{\mathrm{p}} \Delta \mathrm{T}=\mathrm{q}_{\mathrm{p}}=\Delta \mathrm{H}$


## gas expansions

## Process

Work done by the system on the surroundings

Work done on the system by the surroundings
Heat absorbed by the system from the surroundings (endothermic)
Heat absorbed by the surroundings from the system (exothermic)


$$
\left.\begin{array}{l}
\mathbf{T}=\mathbf{c o n s t} \rightarrow \Delta \mathbf{U}=\mathbf{0} \\
\Delta \mathbf{U}=\mathbf{q}^{+\mathbf{w}}\left(1^{\text {st }} \mathbf{l a w}\right)
\end{array}\right\} \mathbf{w}=-\mathbf{q}
$$

- Heat adsorbed by the gas equals the work done by the gas on the
- surroundings. 1 nan expantion, heat is absorbed by the gas for keeping $T$ const. (otherwise it would cool down.)

adiabatic
$\mathrm{q}=$ const. $\rightarrow$ adiabatic equation

$$
\mathbf{P}_{\mathbf{1}} \mathbf{V}_{\mathbf{1}}{ }^{\gamma}=\mathbf{P}_{\mathbf{2}} \mathbf{V}_{\mathbf{2}}{ }^{\gamma} \quad \gamma=\mathbf{c}_{\mathbf{p}} / \mathbf{c}_{\mathbf{v}}
$$

$$
\begin{aligned}
& \left.\begin{array}{l}
\Delta \mathbf{U}=\mathbf{q}+\mathbf{w} \\
\mathbf{q}=\mathbf{0}
\end{array}\right\} \Delta \mathbf{U}=\mathbf{w} \\
& \mathbf{C}_{\mathbf{v}}=\Delta \mathbf{U} / \Delta \mathbf{T} \\
& \mathbf{w}=\mathbf{c}_{\mathbf{v}}\left(\mathbf{T}_{2}-\mathbf{T}_{\mathbf{1}}\right) \begin{array}{c}
\text { expansion } \\
\mathbf{w}<\mathbf{0}
\end{array}
\end{aligned}
$$

Because the gas expands
the internal energy decreases.

## Expansion and compression


Can you discuss this figure in detail? In an exam?
$P_{f} V_{f}{ }^{\gamma}=P_{i} V_{i}{ }^{\gamma}$
for $q=$ const.
$\gamma>1$ steeper curve

## Eminfoppy



Gilblbs

## Entropy definition

## Thermodynamics definition



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



The entropy change of a system is given by the probability ratio of the final and initial states.

## Another version of the $2^{\text {nd }}$ law of thermodynamics

The entropy of an isolated system increases in an irreversible process
and
remains unchanged in a reversible process.
The total entropy can never decrease.

$$
\Delta S=\Delta S_{\text {sys }}+\Delta S_{\text {surr }}=\left\{\begin{array}{c}
0 \text { for reversible } \\
>0 \text { for irreversible }
\end{array}\right\} \text { process }
$$

A system develops towards the state with the greatest probability.

## Short version of the laws

$$
0^{\text {th }} \text { law } \quad \text { Definition of the temperature considering the equilibrium of systems. }
$$

$$
1^{\text {st law }} \quad \Delta U=q+w
$$

$2^{\text {nd }}$ law

$$
\Delta S=\Delta S_{\text {sys }}+\Delta S_{\text {surr }}=\left\{\begin{array}{l}
>\text { for irreversible }
\end{array}\right\} \text { process }
$$

3rd law

$$
\lim _{T \rightarrow 0 K} \Delta S=0
$$

Some properties of the entropy (S)
$\rightarrow$ S is a state function (S does not depend on the path chosen: initial $\rightarrow$ final state)
$\rightarrow$ S is extensive $\quad\left(\mathrm{S}_{\text {tot }}=\mathrm{S}_{1}+\mathrm{S}_{2}+\ldots\right)$
$\rightarrow \Delta_{\text {vap }} \mathrm{S}>0$ and $\Delta_{\text {fus }} \mathrm{S}>0$
$\rightarrow \mathrm{S}_{\text {gas }}>\mathrm{S}_{\text {liquid }}>\mathrm{S}_{\text {solid }}$ (per mole)
$\rightarrow$ S ~ size of a molecule (Why?: \# of degrees of freedom increase with number of atoms)
$\rightarrow \mathrm{P} \rightarrow 0$ then $\mathrm{S} \rightarrow \infty \quad$ (Why? $\Delta \mathrm{S}=\mathrm{nR} \ln \left(\mathrm{V}_{2} / \mathrm{V}_{1}\right)$
$\mathrm{V}_{1}$ : reference volume
$\mathbf{V}_{2} \rightarrow \infty$ for $\mathbf{P} \rightarrow \mathbf{0}$ )
$\rightarrow \mathrm{S} \geq 0$ (Why: $\mathrm{T}=0 \mathrm{~K} \rightarrow \mathrm{w}=1$ (perfect crystal)

$$
\rightarrow \mathrm{S}=\mathrm{k}_{\mathrm{B}} \ln (\mathrm{w})=0 \text {, note that } \mathrm{w}>1
$$

and S increases with temperature )
$\rightarrow$ S increases with temperature

$$
\Delta S_{T}^{\circ}=\Delta S_{298.15}^{\circ}+\int_{298.15}^{T} \frac{\Delta C_{P}^{\circ}}{T^{\prime}} d T^{\prime} \quad \text { Eq.(5.43)-Engel }
$$

$\rightarrow \mathrm{S}_{\text {diamond }}<\mathrm{S}_{\text {graphite }} \quad$ (Why?: High degree of order reduced S )

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$\rightarrow \mathrm{S} \geq 0$

$$
\begin{aligned}
\text { (Why: } T=0 K & \rightarrow \mathrm{w}=1 \text { (perfect crystal) } \\
& \left.\rightarrow \mathrm{S}=\mathrm{k}_{\mathrm{B}} \ln (\mathrm{w})=0, \mathrm{w}>1\right)
\end{aligned}
$$

$\rightarrow$ S increases with temperature

$$
\Delta S_{T}^{\circ}=\Delta S_{298.15}^{\circ}+\int_{298.15}^{T} \frac{\Delta C_{P}^{\circ}}{T^{\prime}} d T^{\prime} \quad \text { Eq.(5.43)-Engel }
$$

$\rightarrow \mathrm{S}_{\text {diamond }}<\mathrm{S}_{\text {graphite }} \quad$ (Why?: High degree of order reduced S)

Some properties of the entropy (S)
$\rightarrow \mathrm{S}_{\text {diamond }}<\mathrm{S}_{\text {graphite }} \quad$ (Why?: High degree of order reduced S )
$\rightarrow$ More complex systems have larger $\mathrm{S}\left(\mathrm{S}_{\mathrm{ozone}}>\mathrm{S}_{\mathrm{O} 2}\right)$
$\rightarrow \mathrm{S}$ increases with the volume of a gas
(Why?: $\Delta S \sim \ln \left(V_{2} / V_{1}\right)$

$$
S\left(\mathbf{N}_{2} @ 0.1 \mathrm{~atm}\right)>S\left(\mathrm{~N}_{2} @ 1 \mathrm{~atm}\right)
$$

$\rightarrow$ Large disorder $\rightarrow$ large entropy

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$\rightarrow$ Entropy change of a reaction

$$
\begin{aligned}
& \mathbf{a A}+\mathbf{b B}+\ldots \rightarrow \mathbf{c C}+\mathbf{d D}+\ldots \\
& \Delta_{\mathbf{r}} \mathrm{S}=\sum \mathbf{v S}(\text { products })-\sum \mathbf{n S}(\text { reactants) } \\
& \Delta S_{R}^{\circ}=\sum_{i} v_{i} S_{i}^{\circ} \quad \text { Eq.(5.41) }
\end{aligned}
$$

## Gibbs energy

```
0}\mp@subsup{}{}{\mathrm{ th law D}}\quad\mathrm{ Definition of the temperature considering the equilibrium of systems.
```

$$
1^{\text {st law }} \quad \Delta U=q+w
$$

$2^{\text {nd }}$ law

$$
\Delta S=\Delta S_{\text {sys }}+\Delta S_{\text {surr }}=\left\{\begin{array}{l}
0 \text { for irreversible }
\end{array}\right\} \text { process }
$$

3rd law

$$
\lim _{T \rightarrow 0 K} \Delta S=0
$$

$\Delta G<0$ for spontaneous process

## Basic Equations

$$
\begin{array}{ll}
\mathbf{d H}=\mathbf{d q}_{\mathbf{P}} & \mathbf{d U}=\mathbf{d q}_{\mathbf{v}} \\
(\mathrm{P}=\text { const }) & (\mathrm{V}=\text { const })
\end{array}
$$

Gibbs energy
Helmholtz energy
$\mathrm{G}=\mathrm{H}-\mathrm{TS}$
for $P$ and $T=$ const
$\mathbf{d G}=\mathbf{d H}$ - TdS
$\mathbf{0} \geq \mathbf{d G}$
$\Delta G=w_{\text {max }}$
$\mathrm{A}=\mathrm{U}-\mathrm{TS}$
for $V$ and $T=$ const dA = dU - TdS
$\mathbf{0} \geq \mathbf{d A}$
$\Delta \mathbf{A}=\mathbf{w}_{\text {max }}$

Follows from $2^{\text {nd }}$ law of thermodynamics

Thermodynamics primer: What is Gibbs telling us? $\quad G:=H-T S$

$$
\Delta S=\Delta S_{\text {sys }}+\Delta S_{\text {surr }}=\left\{\begin{array}{c}
0 \text { for reversible } \\
>0 \text { for irreversible }
\end{array}\right\} \text { process } \begin{aligned}
& \Delta \mathrm{G}=0 \text { at equilibrium } \\
& \Delta \mathrm{G}<0 \text { spontaneous forward reaction }
\end{aligned}
$$


$G:=H-T S$
-TS: heat TAX

$G:=H-T S$
-TS: TAX refund

Discuss this equation.
What is the meaning of the TS term?
What actually is work?
Why is A smaller than U?
$\mathrm{A}=\mathrm{U}$ - 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)

$$
\begin{aligned}
& \text { dAs }=\mathbb{d N U}=\mathbb{T} \mathbb{S}
\end{aligned}
$$

which is energy stored in a disordered way and therefore cannot directly be used to perform work.
$\rightarrow$ Therefore, only the contribution to the internal energy that is not stored in a disordered manner can be transferred into work (that is UTS).

## Phase equilibrium

Phase equilibrium:
freezing: solid-liquid boiling: liquid - gas
crystal structures: graphite - diamond

D How to define the equilibrium? What phase is stable?

Equilibrium condition: $\quad \bar{G}_{\text {phase-1 }}={\overline{G_{\text {phase-2 }}} \quad \text { (molar Gibbs energies) }}$

Rule: Stable phase has lower G
4.40 A certain reaction is known to have a $\Delta_{\mathrm{r}} G^{\mathrm{o}}$ 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 $\Delta \mathrm{G}<0 \rightarrow$ the reaction will always occur

Correct
$\Delta \mathbf{G}>\mathbf{0}$ Reverse reaction may be spontaneous
$\Delta \mathrm{G}<0$ Kinetic limitations

Wrong

## This rule follows from $2^{\text {nd }}$ law of thermodynamics

```
0}\mp@subsup{0}{}{\mathrm{ th law Definition of the temperature considering the equilibrium of systems.}
```

$$
\text { 1st law }^{\Delta U=q+w}
$$

$2^{\text {nd }}$ law 0 for reversible

$$
\Delta S=\Delta S_{\text {sys }}+\Delta S_{\text {sur }}=\left\{\begin{array}{l} 
\\
>0 \text { for irreversible }
\end{array}\right\} \text { process }
$$

$\Delta G<0$ for spontaneous process
$\mu_{i}^{I}>\mu_{i}^{I I}$ 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 <br> temperatures i.e. <br> $\Delta \mathrm{T}>0$ |
| work "flows", work done on <br> a system (pushing a piston) | $\Delta \mathrm{p}>0$ |
| flow of chemical species i <br> from one phase to another | $\Delta \mu>0$ |

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

| State function | Equilibrium |
| :--- | :--- |
| $\Delta \mathrm{T} \approx 0$ | thermal |
| $\Delta \mathrm{p} \approx 0$ | mechanical |
| $\Delta \mu_{\mathrm{i}} \approx 0$ | material |

$\mu$ is called a potential because ..
of the analogy with a mechanical system:


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

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


## Chemical equilibrium

$$
\Delta_{r} G^{0}=-R T \ln \left(K_{P}\right)
$$

$$
\Delta_{r} G^{0}=\Delta_{r} H^{0}-T \Delta_{r} S^{0}
$$

## $K_{p}=K_{p}(T)-$ van't Hoff equation

## Differential version

$$
\frac{d \ln K_{P}}{d T}=-\frac{1}{R} \frac{d\left(\Delta G_{\text {reaction }}^{\circ} / T\right)}{d T}=\frac{\Delta H_{\text {reaction }}^{\circ}}{R T^{2}}
$$

Integrated version

$$
\ln K_{P}\left(T_{f}\right)=\ln K_{P}(298.15 \mathrm{~K})-\frac{\Delta H_{\text {reaction }}^{\circ}}{R}\left(\frac{1}{T_{f}}-\frac{1}{298.15 \mathrm{~K}}\right)
$$

Indefinite integrated version


Jacobus Henricus van 't Hoff

$$
\ln \left(K_{p}\right)=-\frac{\Delta H_{r}^{0}}{R} \frac{1}{T}+\frac{\Delta S_{r}^{0}}{R}
$$

## Le Chatelier's principle

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.


## Phase dinagranos

## Can you discuss these diagrams?



## Phase rule



Constraints / restrictions

## Clausius-Clapeyron Equation



## \&


$\int_{P_{i}}^{P_{f}} \frac{d P}{P}=\frac{\Delta H_{m}^{\text {vaporization }}}{R} \times \int_{T_{i}}^{T_{f}} \frac{d T}{T^{2}}$

$$
\ln \frac{P_{f}}{P_{i}}=-\frac{\Delta H_{m}^{\text {vaporization }}}{R} \times\left(\frac{1}{T_{f}}-\frac{1}{T_{i}}\right)
$$

Solutioms

Vocabulary words:

## Mole <br> fraction



Partial molar quantities

$$
\overline{\boldsymbol{X}}=\left.\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{n}_{\boldsymbol{i}}}\right|_{T, P}
$$

X can be H, G, V

| Partial molar <br> volume | Partial molar <br> Gibbs energy (chemical potential) |
| :--- | :--- |
| $\overline{V_{1}}=\left.\frac{\partial V}{\partial n_{1}}\right\|_{T, P}$ | $\overline{G_{1}}=\left.\frac{\partial G}{\partial n_{1}}\right\|_{T, P}=\mu_{1}$ |
| $V=n_{1} \overline{V_{1}}+n_{2} \overline{V_{2}}+\ldots$ | $G=n_{1} \mu_{1}+n_{2} \mu_{2}+\ldots$ |
| $\sum V_{m} \neq V$ |  |
|  |  |
|  |  |
|  |  |
|  |  |

## Chemical potential - multicomponent systems

$\mu(\mathrm{g})=\mu_{1}{ }^{0}+\mathrm{RT} \ln \left(\mathrm{P} / \mathrm{P}^{0}\right)$ 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

| Rault's law | Henry's law |
| :--- | :--- |
| for solvent | for solute |
| $\mathrm{P}_{1}=\mathrm{x}_{1} \mathrm{P}_{1}^{*}$ | $\mathrm{P}_{2}=\mathrm{K} \mathrm{m}$ |

## 1: solvent

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

> Pressure of solute $\left(\mathrm{CO}_{2}\right), \mathrm{P}_{2}$, 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.

## Pure solvent

solution (solvent + solute)
$\mathbf{P}_{\text {vap }}$ decreases
$\mathrm{T}_{\mathrm{B}}$ increases
$\mathrm{T}_{\mathrm{F}}$
Why? $\mathbf{P}_{\text {vap }}$
$\mathrm{S}_{\text {solution }}>\mathrm{S}_{\text {pure solvent }}$
$\rightarrow \Delta \Delta \mathrm{S}_{\text {mix }}>0 ; \Delta \mathrm{G}_{\text {min }}<0$
Rault's law:
$\rightarrow \Delta \mathrm{P}=\mathrm{X}_{2} \mathrm{P}_{1}{ }^{*}$



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 colute $\rightarrow$ high $\mathrm{c}_{\text {solute }}$
initially


$$
\text { at equilibrium }\left\{\begin{array}{l}
\mu_{1}^{L}=\mu_{1}^{R} \\
\mu_{1}^{*}=\mu_{1}^{*}+R T \ln \left(x_{1}\right)+\Pi \bar{V}
\end{array}\right.
$$

1) Solvent
2) Solute

## Osmotic pressure and engineering

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 $\rightarrow$ solution <br> low $\mathrm{c} \rightarrow$ high c |  |  |
| :---: | :---: | :---: |
|  |  |  |
| Reverse osmosis: | solution <br> water + salt high c | $\rightarrow$ solvent <br> $\rightarrow$ water <br> $\rightarrow$ low c |



