

[TP] What do we need to know to sketch
$\ln(K) = -\Delta H°/R(1/T) + \Delta S°/R$?

17% 1. How K changes with T
17% 2. The sign of $\Delta H°$
17% 3. The sign of $\Delta S°$
17% 4. All of the above
17% 5. Either (1), or (2) and (3)
17% 6. Some other factor(s)

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Response Counter

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Lecture 32 CH102 A2 (MWF 11:15 am)

Friday, April 19, 2019

- Absolute entropy
- Entropy change of reaction
- Free energy change: ΔG

Next lecture: Continue ch17

Notes: Spontaneity: Second law of thermodynamics
http://quantum.bu.edu/courses/ch102-spring-2018/handouts.html

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How to determine ΔS_{sys} for a chemical reaction?

We have seen that we can get ΔS_{sys} for a phase transition using $\Delta S_{tot} = 0$ at the transition temperature.

$\Delta S_{sys} = \Delta H_{sys}/T_{transition}$

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How to determine ΔS_{sys} for a chemical reaction?

Getting ΔS_{sys} for a chemical reaction requires a different approach.

In principle we could get ΔS_{sys} by analyzing changes in particle and energy dispersal as a result of the reaction.

But, in practice, it is easier to get ΔS_{sys} by measuring heat flow between system and surroundings when they are in equilibrium.

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How to determine $\Delta_r S^o$?

At 0 K, for each substance, $W = 1$ and so $S = 0$.

This is known as the third law of thermodynamics.

Starting with $S = 0$ (at $T = 0$), adding a little heat dq,
entropy $dS = dq/{\sim}0K$ will be added, raising T a little bit, say to 1 K.

Adding a little more heat dq,
entropy $dS = dq/{\sim}1K$ will be added, raising T a little bit, say to 2 K.

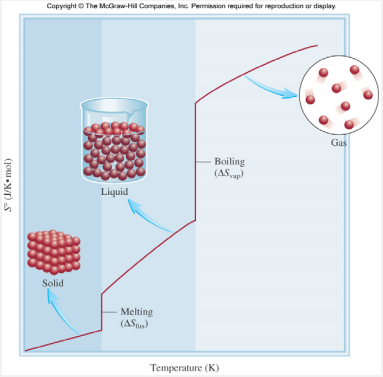
Continuing in this way, up to a final temperature T,
the sum of all of the small additions dS are S for the substance at T.

These values S are called absolute entropies.

Find S at a particular temperature

Make a sketch of how you expect the entropy of water to change with temperature, starting from $S = 0$ at $T = 0$ K and ending at the entropy at $T = 400$ K.

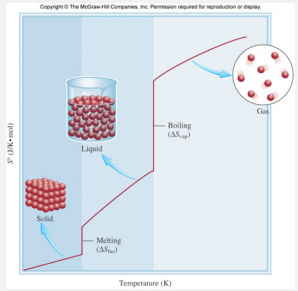
Find S at a particular temperature



Find S at a particular temperature

$S(\text{heating ...}) = \int dq/T = \int c_p \, dT/T$

$S\ (400\ \text{K}) = S(\text{heating solid}) \ldots$
$+ \Delta H_{fus}/T_{fus} \ldots$
$+ S(\text{heating liquid}) \ldots$
$+ \Delta H_{vap}/T_{vap} \ldots$
$+ S(\text{heating gas})$



Find *S* at a particular temperature

Entropies typically are tabulated at 298 K.

These are called standard entropies, $S°$

Note, these absolute entropies, not entropy changes

Selected Thermodynamic Data* at 25 °C

Species	$\Delta_f H°$ (kJ mol^{-1})	$S°$ (J K^{-1} mol^{-1})
Aluminum		
Al(s)	0	28.3
$AlCl_3(s)$	−705.63	109.29
$Al_2O_3(s)$	−1675.7	50.92
Barium		
$BaCl_2(s)$	−858.6	123.68
$BaCO_3(s)$	−1213	112.1
BaO(s)	−548.1	72.05
$BaSO_4(s)$	−1473.2	132.2
Beryllium		
Be(s)	0	9.5
$Be(OH)_2(s)$	−902.5	51.9

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How to get entropy change of reaction, $\Delta_r S°$?

1. Get absolute entropies $S°$ (Mahaffy et al., Appendix D)
2. $\Delta_r S° = S_{\text{products}} - S_{\text{reactants}}$

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Entropy of reaction, $\Delta S°_r$

$\Delta_r S° = S_{\text{products}} - S_{\text{reactants}}$

Rules of thumb:

- If more gas moles formed, $\Delta_r S°$ large and positive
- If more gas moles consumed, $\Delta_r S°$ large and negative
- If gas moles unchanged, $\Delta_r S°$ small but positive or negative

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$\Delta_r S°$ = $S°$(products) − $S°$(reactants)

$2\ Zn(s) + O_2(g) \rightarrow 2\ ZnO(s)$

$\Delta_r S° = 2 \times 43.7 - (2 \times 41.6 + 205.0) = -200.8$ J/K

$\Delta n_g = -1$, so $\Delta_r S°$ is large and negative

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$

$\Delta_r S° = 2 \times 210.8 - (191.6 + 205.0) = +25$ J/K

$\Delta n_g = 0$, so $\Delta_r S°$ is small

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Free energy change, ΔG

In electrochemistry (lecture 24) we learned that free energy change is the work than can be done on the surroundings (excluding any pressure volume work).

For an electrochemical cell, this work available to the surroundings is

$$\Delta G_{\text{cell}} = -n_e F E_{\text{cell}}$$

The fundamental, general expression for free energy change—the work available to the surroundings—is

$$\Delta G = -T\Delta S_{\text{tot}}$$

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Free energy change, ΔG

The general expression for free energy change can be rewritten in terms on the system enthalpy change and system entropy change,

$$\Delta G = -T\Delta S_{\text{tot}}$$
$$= -T\Delta S_{\text{sur}} - T\Delta S_{\text{sys}}$$
$$= +\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

The components of ΔG are usually written with "sys" omitted …

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

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System-only spontaneity measure

ΔG depends only on "sys" quantities, but it reflects ΔS_{tot}.

If $\Delta G < 0$, then spontaneous ($\Delta S_{\text{tot}} > 0$) and process provides work

If $\Delta G = 0$, then equilibrium ($\Delta S_{\text{tot}} = 0$) and no work is involved

If $\Delta G > 0$, then non-spontaneous ($\Delta S_{\text{tot}} < 0$) and process requires work

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