[TP] For steam → liquid water, $\Delta S_{tot} = -\frac{\Delta H_{vap}}{373\text{ K}} + \frac{\Delta H_{vap}}{T} = \Delta H_{vap}\left(-\frac{1}{373\text{ K}} + \frac{1}{T}\right)$.
At $T = 100°C = 373\text{ K}$, ΔS_{tot} evaluates to ...

0%	1.	< 0
100%	2.	$= 0$
0%	3.	> 0
0%	4.	Note sure

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Lecture 12 CH131 Summer 1 2021

Wednesday, June 16, 2021

- Complete: Spontaneity of phase transitions
- Absolute entropy ($S°$)
- Relative entropy values
- Entropy change of reaction ($\Delta S°_{rxn}$)
- Free energy change: ΔG

Next: Effect of temperature on spontaneity; Chapter 24: Chemical equilibrium

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steam → liquid water

Since $\Delta S_{sys} < 0$ and $\Delta S_{sur} > 0$, their contributions to

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$$

oppose one another.

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steam → liquid water

What are the values of ΔS_{sys} and ΔS_{sur}?

Since condensation releases heat ($q_{sys}) = -\Delta H_{vap}$ to the surroundings, the entropy of the surroundings increases during condensation,

$$\Delta S_{sur} = \frac{q_{sur}}{T} = \frac{-q_{sys}}{T} = \frac{\Delta H_{vap}}{T} > 0$$

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steam → liquid water

But since $\Delta S_{\text{tot}} = 0$ at $T = 100°\text{C}$, the system entropy change is the special value

$$\Delta S_{\text{sys}} = -\Delta S_{\text{sur}}(100°\text{C}) = -\frac{\Delta H_{\text{vap}}}{373\ \text{K}} < 0$$

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steam → liquid water

Putting these value together, we get

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = -\frac{\Delta H_{\text{vap}}}{373\ \text{K}} + \frac{\Delta H_{\text{vap}}}{T}$$

This result shows that it is the entropy change of the surroundings that determines when condensation of steam is spontaneous.

That is, it is the temperature at which heat is transferred to the surroundings that determines when $|\Delta S_{\text{sur}}| > |\Delta S_{\text{sys}}|$.

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[TP] For steam → liquid water, $\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{vap}}}{373\ \text{K}} + \frac{\Delta H_{\text{vap}}}{T} = \Delta H_{\text{vap}}\left(-\frac{1}{373\ \text{K}} + \frac{1}{T}\right)$.
At $T = 100°\text{C} = 373\ \text{K}$, ΔS_{tot} evaluates to …

373 K

- 0% 1. < 0
- 100% 2. $= 0$
- 0% 3. > 0
- 0% 4. Note sure

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[TP] For steam → liquid water, $\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{vap}}}{373\ \text{K}} + \frac{\Delta H_{\text{vap}}}{T} = \Delta H_{\text{vap}}\left(-\frac{1}{373\ \text{K}} + \frac{1}{T}\right)$.
At $T = 94°\text{C} = 367\ \text{K}$, ΔS_{tot} evaluates to …

367K

- 0% 1. < 0
- 0% 2. $= 0$
- 100% 3. > 0
- 0% 4. Note sure

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[TP] For steam → liquid water, $\Delta S_{tot} = -\frac{\Delta H_{vap}}{373\text{ K}} + \frac{\Delta H_{vap}}{T} = \Delta H_{vap}\left(-\frac{1}{373\text{ K}} + \frac{1}{T}\right)$.
At T = 106°C = 379 K, ΔS_{tot} evaluates to ...

379 K

100%	1.	< 0
0%	2.	= 0
0%	3.	> 0
0%	4.	Note sure

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Spontaneity = increase in total entropy

Spontaneity means that ...

$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur} > 0$

Spontaneity does not require that ...

$\Delta S_{sys} > 0$ or $\Delta S_{sur} > 0$

The separate roles of ΔS_{sys} and ΔS_{sur} account for why steam condenses and water boils.

l → s, s → l; s → g, g → s

The same approach works for melting and for sublimation.

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

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

$\Delta S_{sys} = -\frac{\Delta H_{transition}}{T_{transition}}$, where $T_{transition} = T_{melt}, T_{boil}$, or $T_{sublime}$,

since at that temperature the two phases are in equilibrium so $\Delta S_{tot} = 0$.

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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, W_p and W_e, as a result of the chemical transformation.

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

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

This is analogous to what we did for condensation of steam to get

$$\Delta S_{tot} = 0 = +\frac{\Delta H_{vap}}{373\text{ K}} + \Delta S_{sys} \rightarrow \Delta S_{sys} = -\frac{\Delta H_{vap}}{373\text{ K}}$$

since at 373 K = 100°C the system and surroundings are in equilibrium.

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How to determine ΔS^o_{rxn} ?

The essential starting point is that at 0 K, for each substance,

$W = 1$ and so $S = 0$.

This is known as the third law of thermodynamics.

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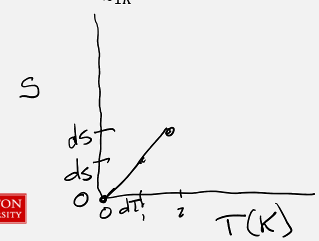
How to determine ΔS^o_{rxn} ?

Starting with $S = 0$ (at $T = 0$), adding a little heat dq_1,
entropy $dS_1 = \frac{dq_1}{\sim 0K}$ will be added, raising T a little bit, say to 1 K.

Adding a little more heat dq_2,
entropy $dS_2 = \frac{dq_2}{\sim 1K}$ will be added, raising T another little bit, say to 2 K.



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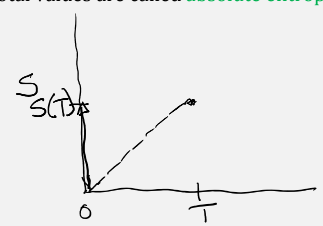
How to determine ΔS^o_{rxn} ?

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,

$$S^o(T) = dS_1 + dS_2 + \cdots + dS_n$$

These total values are called absolute entropies (S^o) at temperature T.



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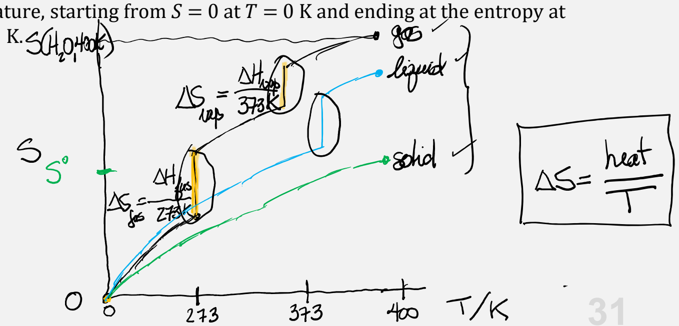
Find *S* at a particular temperature

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.



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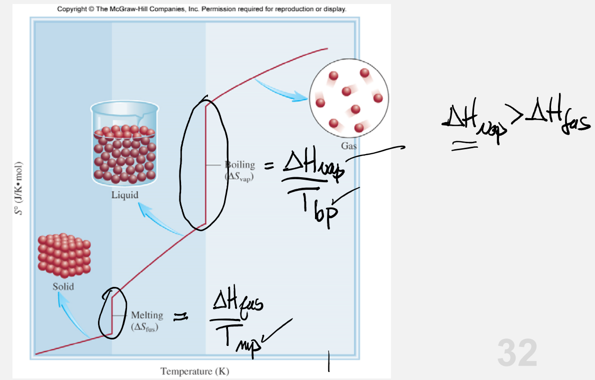
Find *S* at a particular temperature



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Find *S* at a particular temperature

Absolute entropies typically are tabulated at 298 K.

Note, these are entropies, not entropy changes.

Substance	$S°$/ J·K^{-1}·mol^{-1}	$\Delta H_f°$/ kJ·mol^{-1}	$\Delta G_f°$/ kJ·mol^{-1}
$H_2O_2(l)$	109.6	–187.8	–120.4
$H_2S(g)$	205.8	–20.6	–33.4
$N(g)$	153.3	472.7	455.5
$N_2(g)$	191.6	0	0
$NH_3(g)$	192.8	–45.9	–16.4
$N_2H_4(l)$	121.2	50.6	149.3
$NO(g)$	210.8	91.3	87.6
$NO_2(g)$	240.1	33.2	51.3
$N_2O(g)$	220.0	81.6	103.7
$N_2O_4(g)$	304.4	11.1	99.8
$N_2O_5(s)$	178.2	–43.1	113.9
$Na(g)$	153.7	107.5	77.0

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Relative entropy values

In assessing relative entropy values at 25°C, note the following qualitative values.

In general, liquids have greater entropy than solids, because of the contribution $\frac{\Delta H_{\text{fusion}}}{T}$ to their total entropy

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Relative entropy values

In general, gases have greater entropy than liquids, because of the contribution $\frac{\Delta H_{vap}}{T}$ to their total entropy.

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Relative entropy values

In general, the more electrons in the electron clouds, the more energy levels and so the more ways (W_e) energy can be stored.

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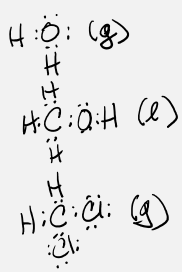
[TP] Rank the following in order of increasing standard molar entropy, $S°$, at 25°C: $H_2O(g)$, $CH_3OH(l)$, $CH_2Cl_2(g)$

0%	1.	$S°[H_2O(g)] < S°[CH_3OH(l)] < S°[CH_2Cl_2(g)]$
100%	2.	$S°[CH_3OH(l)] < S°[H_2O(g)] < S°[CH_2Cl_2(g)]$
0%	3.	$S°[CH_3OH(l)] < S°[CH_2Cl_2(g)] < S°[H_2O(g)]$
0%	4.	$S°[H_2O(g)] < S°[CH_2Cl_2(g)] < S°[CH_3OH(l)]$
0%	5.	$S°[CH_2Cl_2(g)] < S°[H_2O(g)] < S°[CH_3OH(l)]$
0%	6.	$S°[CH_2Cl_2(g)] < S°[CH_3OH(l)] < S°[H_2O(g)]$
0%	7.	None of the above
0%	8.	Note sure



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Relative entropy values

Consider following in order of increasing standard molar entropy, $S°$, at 25°C: $H_2O(g)$, $CH_3OH(l)$, $CH_2Cl_2(g)$.

$S°[CH_3OH(l)] = 126.8$ J/(K mol)

$S°[H_2O(g)] = 188.8$ J/(K mol)

$S°[CH_2Cl_2(g)] = 270.2$ J/(K mol)

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How to get entropy change of reaction, $\Delta S°_{rxn}$?

Using tabulations of absolute entropies, $S°$, we can calculate the entropy change of any reaction:

1. Get absolute entropies $S°$
2. $\Delta S°_{rxn} = \Sigma(S°_{products}) - \Sigma(S°_{reactants})$

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[TP] Which of the following is the correct expression for $\Delta S°_{rxn} = \Sigma(S°_{products}) - \Sigma(S°_{reactants})$

Type equation here.of the reaction $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

0%	1.	$+\Delta S°_f(C,s) + \frac{1}{2}\Delta S°_f(O_2,g) - \Delta S°_f(CO,g)$
8%	2.	$-\Delta S°_f(C,s) - \frac{1}{2}\Delta S°_f(O_2,g) + \Delta S°_f(CO,g)$
8%	3.	$+\Delta S°_f(CO,g)$
0%	4.	$-\Delta S°_f(CO,g)$
0%	5.	$+S°(C,s) + \frac{1}{2}S°(O_2,g) - S°(CO,g)$
67%	6.	$-S°(C,s) - \frac{1}{2}S°(O_2,g) + S°(CO,g)$
0%	7.	$+S°(CO,g)$
0%	8.	$-S°(CO,g)$
17%	9.	Note sure

$H_2(g) \rightarrow 2H(g)$

$1S°(H_2,g)$ $2S°(H,g)$

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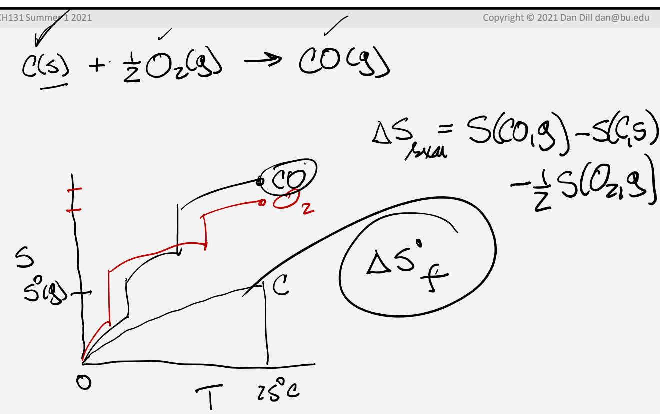

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Entropy of reaction, $\Delta S°_{rxn}$

$\Delta S°_{rxn} = \Sigma(S°_{products}) - \Sigma(S°_{reactants})$

Rules of thumb:

- If more gas moles formed, $\Delta S°_{rxn}$ large and positive
- If more gas moles consumed, $\Delta S°_{rxn}$ large and negative
- If gas moles unchanged, $\Delta S°_{rxn}$ small but positive or negative

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$\Delta S^{o}_{rxn} = \Sigma(S^{o}\text{products}) - \Sigma(S^{o}\text{reactants})$

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

$\Delta S^{o}_{rxn} = 2 \times 43.7 - (2 \times 41.6 + 205.0) = -200.8$ J/K

$\Delta n_g = -1$, so ΔS^{o}_{rxn} is large and negative

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$\Delta S^{o}_{rxn} = \Sigma(S^{o}\text{products}) - \Sigma(S^{o}\text{reactants})$

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

$\Delta S^{o}_{rxn} = 2 \times 210.8 - (191.6 + 205.0) = +25$ J/K

$\Delta n_g = 0$, so ΔS^{o}_{rxn} is small

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An alternative criterion of spontaneity

Quantifying spontaneity, we have learned so far:

$W \rightarrow S = k_B \ln(W) \rightarrow \Delta S = k_B \ln\left(\frac{W_f}{W_i}\right)$

$\Delta S_{tot} = \Delta S_{sur} + \Delta S_{sys}$

$\Delta S_{sur} = \frac{q_{sur}}{T} = -\frac{\Delta H_{sys}}{T}$

$\Delta S_{tot} = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}$

ΔG = free energy change.

$\Delta H_{sys} \rightarrow \Delta H_{rxn} = \Sigma \Delta H^{o}_{f}(\text{prod}) - \Sigma \Delta H^{o}_{f}(\text{react})$

$\Delta S_{sys} \rightarrow \Delta S_{rxn} = \Sigma S^{o}(\text{prod}) - \Sigma S^{o}(\text{react})$

$\Delta G \equiv -T\Delta S_{tot}$

$\Delta G_{sys} \equiv +\Delta H_{sys} - T\Delta S_{sys}$

$\Delta S_{tot} > 0,\ \Delta G_{sys} < 0$

$\Delta S_{tot} < 0,\ \Delta G_{sys} > 0$

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An alternative criterion of spontaneity

For phase transitions:

$\Delta S_{tot} = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}$

$= -\frac{\Delta H_{transition}}{T} + \frac{\Delta H_{transition}}{T_{transition}}$

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An alternative criterion of spontaneity

For chemical reactions:

$$\Delta S_{tot} = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}$$

$$= -\frac{\Delta H_{rxn}}{T} + \Delta S_{rxn}$$

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[TP] While ΔS_{tot} takes into account entropy change in both the surroundings and the system, the expression $\Delta S_{tot} = -\frac{\Delta H_{rxn}}{T} + \Delta S_{rxn}$ means that for chemical reactions, …

27%	1.	the entropy change of the surroundings is not important
36%	2.	then entropy change of the surroundings still plays a role
9%	3.	only exothermic reactions are spontaneous
27%	4.	Further information needed

ΔS_{surr}

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

$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T}$

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An alternative criterion of spontaneity

While the expression

$$\Delta S_{tot} = -\frac{\Delta H_{rxn}}{T} + \Delta S_{rxn}$$

has only properties of the system, always remember that $-\frac{\Delta H_{rxn}}{T}$ is the entropy change of the surroundings.

This shows that spontaneity is favored by exothermic reactions ($\Delta H_{rxn} < 0$) because they increase the entropy of the surroundings.

However, whether a reaction is spontaneous ($\Delta S_{tot} > 0$) also depends on ΔS_{rxn}.

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Free energy change, ΔG

To emphasize that we only have to know the system quantities ΔH_{rxn} and ΔS_{rxn}, the free energy change of reaction is defined as

$$-T\Delta S_{tot} = \Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$

The components of ΔG are usually written with "rxn" (or "sys") omitted …

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

It turns out that free energy change is the work than can be done on the surroundings (excluding any pressure volume work), and so tells us how much work we can get from a chemical transformation.

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System-only spontaneity measure

ΔG depends only on system quantities, but it is equivalent to 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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Problem 7e and 8e 13.31

31. Ethanol's enthalpy of vaporization is 38.7 kJ mol^{-1} at its normal boiling point, 78°C. Calculate q, w, ΔU, ΔS_{sys}, and ΔG when 1.00 mol ethanol is vaporized reversibly at 78°C and 1 atm. Assume that the vapor is an ideal gas and neglect the volume of liquid ethanol relative to that of its vapor.

$\Delta U = q + w$ | If V = const, $w = 0$, $\Delta U = q_V$; If P = const, $w \neq 0$

$Et(l) \rightarrow Et(g)$ $\Delta H_{vap} = \frac{38.7\ kJ}{mol}$

$q = q_P = \text{moles} * \Delta H = 1.00\ mol * \frac{38.7\ kJ}{mol} = 38.7\ kJ$

$w_{PV} = -P_{ext}\Delta V = -1\ atm\ \Delta V = -\Delta n RT = -(1\ mol)\left(8.314 \frac{J}{mol\ K}\right)(273+78)K = -2920\ J$

$\Delta U = q + w = 35800\ J$

$q_P = 38700\ J$, $w_{PV} = -2920\ J$ | $\Delta S_{sys} = \frac{\Delta H_{sys}}{T} = \frac{38700\ J}{(273+78)K} > 0$

$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$

$= 38700\ J - (273+78)K * \frac{38700\ J}{(273+78)K}$

$= 0$ = equilibrium.

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