

Benjamin Thomson, Lord Kelvin

Chemistry BC2001x: General Chemistry I



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Lecture 22: Tuesday December 8, 2009

Topic: **Thermodynamics II:**
Entropy. Gibbs Free Energy and Equilibrium

Pick up **graded exam 3** (results and answers on [www](#)).

Study guide for the final exam is on-line
(to save paper): read it carefully!

The data sheets that will be included with
the final exam will soon be posted on the web.
You will also, of course, be given a periodic table.

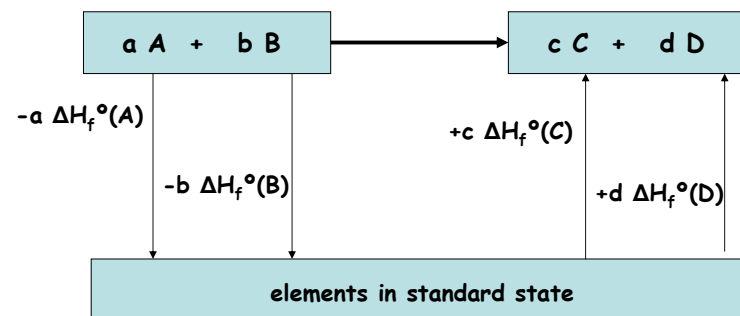
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Using Standard enthalpies of formation

For any reaction, imagine

- 1) converting reactants to elements in standard state
- 2) converting these elements into products.

ΔH for the direct reaction is the sum of these ΔH 's



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THERMODYNAMIC DATA		CHEMISTRY BC2001x			
SUBSTANCE	ΔH_f° (kJ/mole)	ΔG_f° (kJ/mole)	S° (J/K-mole)		
Br ₂ (g)	30.907	3.144	245.35		
Br(l)	111.88	82.43	174.91		
HBr(g)	-36.40	-53.43	198.59		
CaO(s)	-635.09	-604.05	39.75		
CaCO ₃ (s)	-1206.92	-1128.84	92.9		
CO(g)	-110.525	-137.15	197.56		
CO ₂ (g)	-393.51	-394.36	213.64		
CH ₄ (g)	-74.81	-50.75	186.15		
C ₂ H ₂ (g)	226.73	209.20	200.83		
C ₂ H ₄ (g)	52.26	68.12	219.45		
C ₂ H ₆ (g)	-84.68	-32.89	229.49		
C ₃ H ₈ (g)	82.927	129.66	269.2		
CH ₃ OH(l)	-238.66	-166.35	126.8		
CH ₃ CH ₂ OH(l)	-277.69	-174.89	160.7		
HCl(g)	-92.307	-95.299	186.80		
HF(g)	-271.1	-273.2	173.67		
H(g)	217.965	203.263	114.60		
Fe ₂ O ₃ (s)	-824.2	-742.2	87.40		
PbO ₂ (s)	-277.4	-217.4	68.6		
PbS(s)	-100.4	-98.7	91.2		
Hg(g)	61.317	31.853	174.85		
NO(g)	90.25	86.55	210.652		
NO ₂ (g)	33.8	51.29	239.95		
NH ₃ (g)	-46.11	-16.48	192.34		
N ₂ H ₄ (g)	95.40	159.35	238.47		
NH ₄ NO ₃ (s)	-365.56	-184.02	151.08		
O ₃ (g)	142.7	163.2	238.82		
H ₂ O(g)	-241.82	-228.59	188.72		
H ₂ O(l)	-285.83	-237.18	69.91		
SO ₂ (g)	-296.830	-300.194	248.11		
SO ₃ (g)	-395.72	-371.08	256.65		
ELEMENT	S° (J/K-mole)	ELEMENT	S° (J/K-mole)	ELEMENT	S° (J/K-mole)
Al(s)	28.33	Cl ₂ (g)	222.96	Fe(s)	27.28
Br ₂ (l)	152.23	F ₂ (g)	202.67	Hg(l)	76.02
Ca(s)	41.42	H ₂ (g)	130.57	N ₂ (g)	191.50
C(graphite)	5.740	I ₂ (s)	116.14	O ₂ (g)	205.03

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Entropy S

Formal definition: if T is constant $\Delta S = q/T$

(We will NOT use this for calculations this term.)

q has units of energy, so S has units of energy/temp

S is extensive: divide by moles to get S per mole.

ΔS values often given in units **J/K-mole**

Like E and H, S is a state function.

As described briefly earlier:

Entropy measures the disorder in a system

$\Delta S > 0$ for melting, $\Delta S > 0$ for boiling.

$S(\text{solid}) < S(\text{liquid}) \ll S(\text{gas})$

Second law of thermodynamics: entropy increases in all spontaneous changes in isolated systems.

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The direction of spontaneous change

In simple mechanical systems, spontaneous changes move towards lower energy (balls roll downhill.)

Spontaneous changes favor

lower enthalpy ($\Delta H < 0$) and
higher entropy ($\Delta S > 0$) (2nd Law)

Note that chemical reactions are not isolated, so it is possible for ΔS to be negative, so long as ΔS for the surroundings is a larger positive value.

How do these combine?

	$\Delta H > 0$	$\Delta H < 0$
$\Delta S > 0$?	YES
$\Delta S < 0$	NO	?

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New thermodynamic function G

Define Gibbs Free Energy: $G = H - TS$

Like E and H , an energy. Typical units: kJ/mole

Like E , H , T , and S , G is a state function.

If T is constant, $\Delta G = \Delta H - T\Delta S$

At constant temperature and pressure,

ΔG tells you which way any process will occur:

$\Delta G < 0$: the process is spontaneous as written
the reaction will proceed towards products

$\Delta G > 0$: the reverse process is spontaneous

$\Delta G = 0$: the system is at equilibrium

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Balancing enthalpy and entropy

Consider an endothermic process in which entropy increases: $\Delta H > 0$ and $\Delta S > 0$

Example: melting and boiling

Enthalpy favors reactants, entropy products

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

Since the ΔS term is multiplied by T ,

at low T , the ΔH term dominates so $\Delta G > 0$

at high T , the ΔS term dominates so $\Delta G < 0$

As T increases, solids melt, liquids boil.

At the melting point

$$\Delta G = 0 = \Delta H - T\Delta S, \text{ so } \Delta H = T\Delta S$$

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The Three Laws of Thermodynamics

In isolated systems

(nothing exchanged between system and surroundings):

1. Energy is conserved in all processes
2. Entropy increases in spontaneous processes
3. ΔS for all processes $\rightarrow 0$ as $T \rightarrow 0$ K

or stated more whimsically

1. You can never win: at best you can break even.
2. You can break even only at absolute zero
3. You cannot get to absolute zero.

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Third Law Entropies

As with enthalpy, we want a way to assign S values to substances. But again, only ΔS can be measured.

We could again define S at 25°C for elements, and from them get S for compounds.

From the third law, $\Delta S = 0$ for all reactions at 0°K , so it is convenient to use a system that says $S^\circ = 0$ for all (pure perfectly crystalline) substances at 0°K .

Thus S° for any substance at 25°C is ΔS for warming the substance from 0°K to 25°C (at 1 atm.)

S° values are tabulated: see tables (no Δ !)

S° for elements in standard states are not zero: they are given in a separate table at the end.

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ΔG° and equilibrium constants

From S° values, calculate ΔS° for reaction.

From ΔH_f° values, calculate ΔH° for reaction.

Calculate $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

(may also find this from tables of ΔG_f°)

BE CAREFUL WITH UNITS (kJ vs J)

The $^\circ$ are important: this ΔG is for the reaction at standard conditions: pressures = 1 atm, []'s = 1 M.

Do not omit them!

$\Delta G^\circ = -RT \ln K_{eq} = -2.303 RT \log K_{eq}$

$\log K_{eq} = -\Delta G^\circ / (2.303 RT)$

At 25°C , $(2.303 RT) = 5.70804 \text{ kJ/mole}$

(this will be given in data tables for final.)

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ΔG and ΔG°

If the system is NOT at standard conditions, then we need ΔG , not ΔG° , to see what will occur.

How are they related? $\Delta G = \Delta G^\circ + RT \ln Q$

At equilibrium, $\Delta G = 0$ and $Q = K$, so this gives

$$\Delta G^\circ = -RT \ln K_{eq}$$

At standard conditions, $Q = 1$, so $\Delta G = \Delta G^\circ$

Relate to electrochemical cells:

The connection is through $\Delta G = -n \mathcal{F} \Delta \mathcal{E}$

$$-n \mathcal{F} \Delta \mathcal{E} = -n \mathcal{F} \Delta \mathcal{E}^\circ + RT \ln Q$$

$$\Delta \mathcal{E} = \Delta \mathcal{E}^\circ - (RT/n\mathcal{F}) \ln Q \quad \text{Nernst Equation}$$

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Predicting which way reactions go

opposite process will occur	equilibrium	SPONTANEOUS as written
$Q > K$	$Q = K$	$Q < K$
$\Delta G > 0$	$\Delta G = 0$	$\Delta G < 0$
$\Delta \mathcal{E} < 0$	$\Delta \mathcal{E} = 0$	$\Delta \mathcal{E} > 0$

To predict whether a reaction will occur away from standard conditions, you could first calculate ΔG° , from it calculate ΔG : $\Delta G = \Delta G^\circ + RT \ln Q$, and look at the sign;

but it is probably easier just to calculate Q and compare it with K . The answer should be the same.

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