

Don't forget to do my course evaluation!

electronic Course Instructor Survey (eCIS)

I thoroughly enjoy reading all feedback

Unit 4 Exam Review

THERMODYNAMICS

Thermodynamics Equations

$$\Delta U = U_f - U_i$$

$$\Delta U = q + w$$

$$q = m C_s \Delta T$$

$$q = n C_m \Delta T$$

$$q = m \Delta H_{\text{trans}}$$

$$q = n \Delta \overline{H}_{\text{trans}}$$

$$w = -P_{\text{ext}} \Delta V$$

$$w = -\Delta n_{\text{gas}} RT$$

$$\Delta n_{\text{gas}} = (\# \text{mol gas prod}) - (\# \text{mol gas react})$$

$$H = U + PV$$

$$\Delta H = \Delta U + P \Delta V$$

$$\Delta U = \Delta H - P \Delta V$$

$$\Delta U = \Delta H - \Delta n RT$$

$$\Delta H = q_p$$

$$\Delta U = q_v$$

$$q_{\text{cal}} = -q_{\text{sys}}$$

$$q_{\text{cal}} = C_{\text{cal}} \Delta T$$

$$q_{\text{cal}} = m_{\text{water}} C_{s,\text{water}} \Delta T + C_{\text{hardware}} \Delta T$$

$$\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ (\text{products}) - \sum n \Delta H_f^\circ (\text{reactants})$$

$$\Delta H_{\text{rxn}}^\circ \approx \sum n \Delta H_{\text{bond}}^\circ (\text{breaking}) - \sum n \Delta H_{\text{bond}}^\circ (\text{making})$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$S = k \ln \Omega$$

$$\Delta S = q_{\text{rev}} / T$$

$$\Delta S = n C_p \ln(T_f / T_i)$$

$$\Delta S_{\text{trans}} = \Delta H_{\text{trans}} / T_{\text{trans}}$$

$$\Delta S_{\text{rxn}}^\circ = \sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reactants})$$

$$G = H - TS$$

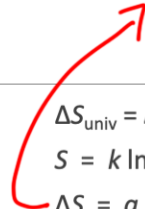
$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ (\text{products}) - \sum n \Delta G_f^\circ (\text{reactants})$$

$$\Delta H = T_{\text{eq}} \Delta S$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}}$$

$\rightarrow \frac{J}{g}$



What to do before the exam tomorrow...

Assuming you've already worked hard to have a conceptual foundation for everything...

1. Print and annotate formulas you will memorize
2. Redo the homework PDFs (available on Dr. McCord's website and Dr. B's Canvas)
3. Bonus Problem Set 1: 1, 4, 5, 20, 23, 25, 27, 28, 29, 42, 43, 51, 69
4. Bonus Problem Set 2: 5, 6, 9, 10, 11, 14, 16, 17, 20
5. Be able to work ALL problems from my reviews

}

Thermo Exam Common Mistakes

1. Sign convention is extremely important

- Know how we use vocabulary to denote sign and what that means
- Endothermic, work done on system, compression, spontaneous, equilibrium, (and more) are all terms we can give you sign without a value
- The heat measured by the calorimeter (q_{cal}) is equal to the heat of the surroundings; or $q_{\text{cal}} = -q_{\text{sys}}$

2. Know how to convert between kJ/mol, kJ, kJ/g, etc.

- Students do a great job of memorizing formulas, but then miss questions because they don't do the final step of scaling to the correct amount
- For example: be able to do conversions like going from ΔH_{rxn} (intensive property) and ΔH (extensive property) of a given amount

3. Know how to look at a question and get started (good thermodynamics intuition!)

- Do *more* than memorize the formulas. Know how to annotate the full list and explain when you use them to solve for a question

4. Subscript Convention

- Understand the differences between being asked for the ΔS_{sys} versus ΔS_{surr} or $\Delta S_{\text{universe}}$, etc.

Big Picture of Thermodynamics

Our universe has finite energy and is constantly expanding. In other words, our universe has a finite capacity to do work (to do work, we need to lower the free energy, $\Delta G < 0$) and the entropy of the universe is always increasing ($\Delta S_{\text{total}} > 0$).

- A **Spontaneous Reaction** is a reaction that proceeds without the continual input of energy because it follows the natural tendency of the universe (reaching a lower energy, more dispersed state).

1) $\Delta G < 0$

2) $\Delta S_{\text{total}} > 0$

3) $\Delta U_{\text{universe}} = 0$

$\Delta H_{\text{sys}} < 0, \Delta S_{\text{sys}} > 0 \rightarrow$ always spontaneous

Just one... \rightarrow T-dependent

Spontaneity: Entropy and Free Energy

- The second law of thermodynamics states that the entropy of the universe is always increasing.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

- This law gives us three conditions for ΔS_{total} :

1. $\Delta S < 0$ (negative) ; your reaction is nonspontaneous
2. $\Delta S = 0$ (zero) ; your reaction is at equilibrium / reversible
3. $\Delta S > 0$ (positive) ; your reaction is spontaneous

- The equation for the second law can be rewritten for free energy with respect to the system only

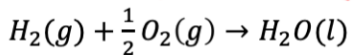
$$\Delta G = \Delta H - T\Delta S$$

- This law gives us three conditions for ΔG_{rxn} :

1. $\Delta G < 0$ (negative) ; your reaction is spontaneous
2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium
3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous

Big Picture Exam Question

Hydrogen spontaneously combusts with oxygen to form liquid water at standard conditions.



What are the signs of:

1. $\Delta H = (-)$
2. $w = (+)$
3. $\Delta S_{\text{sys}} = (-)$
4. $\Delta S_{\text{surr}} = (+)$
5. $\Delta S_{\text{total}} = (+)$
6. $q = (-)$
7. $\Delta G^\circ = (-)$

What are the conclusions you can make about...

$\Delta U = \Delta H - \Delta nRT$ $q + w$

ΔU vs ΔH ? $\Delta U > \Delta H$

ΔS_{surr} vs ΔS_{sys} ? $|\Delta S_{\text{surr}}| > |\Delta S_{\text{sys}}|$ $\Delta S_{\text{total}} > 0$

When is this reaction spontaneous / non-spontaneous?

$\Delta H (-)$ $\Delta S (-)$ (ΔG is negative)
 $\Delta G = \Delta H - T\Delta S$ @ Lower T

First Law

THE ENERGY OF THE UNIVERSE IS ALWAYS CONSERVED

The First Law of Thermodynamics

- The energy of the universe is always conserved
- The conclusions of this law are:
 1. The internal energy change of the system is the sum of the heat and work
 2. The internal energy loss of the system is the equal to energy gain of the surroundings
 3. The internal energy change of the universe is zero and there is no energy or matter leaving

$$q_{sys} = -q_{surr}$$

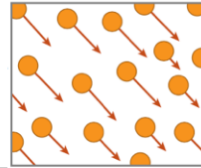
$$w_{sys} = -w_{surr}$$

$$\Delta U_{sys} = \underline{q + w}$$

$$\Delta U_{sys} = -\Delta U_{surr} \quad *$$

$$\Rightarrow \Delta U_{universe} = 0$$

First Law of Thermodynamics



$$\Delta U_{sys} = q + w$$

Work is the energy derived from **organized molecular motion**

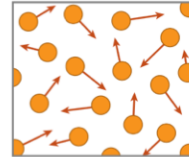
$w > 0$; work energy in, work is done on the system (+), compression, $\Delta V < 0$, $\Delta n < 0$

$w < 0$; work energy out, work is done by the system (-), expansion, $\Delta V > 0$, $\Delta n > 0$

Heat is the energy derived from **random molecular motion** (always travels from high T to low T)

$q > 0$; endothermic (+), heat is absorbed

$q < 0$; exothermic (-), heat is released



Work Calculations

In chemistry we calculate work based on a change in volume at constant pressure.

- Provided a change in volume at constant pressure, the value of work is:
$$w = -P\Delta V \times \left(\frac{101.325 \text{ J}}{1 \text{ atm} \cdot \text{L}}\right)$$
- However, if we are not provided a change in volume, we must rely on the change in gas moles of the balanced chemical reaction (Δn) to solve for work:

$$w = -\Delta nRT$$

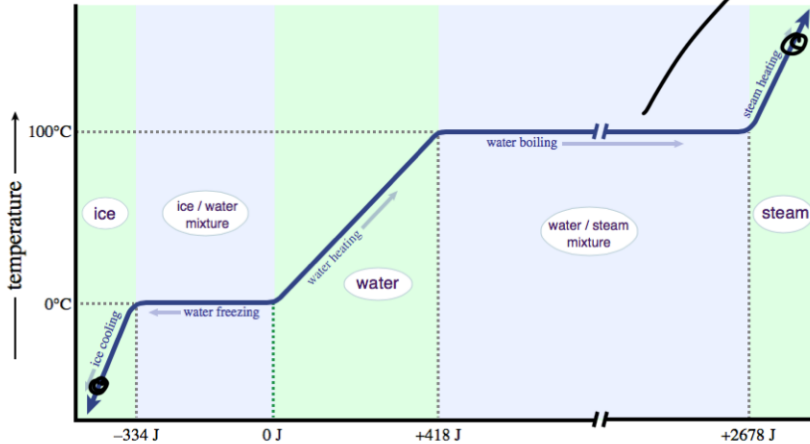
Remember from the first unit that liquids, solids, and aqueous phase compounds contribute negligible volumes to the system.

$$w = -P\Delta V = -\Delta nRT$$

Δn is **ONLY** the change in gas moles!

Heat Flow: Heating Curves

$$\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$$



Heat of a Temperature Change

$$q = mC_s\Delta T$$

Heat of a Phase Change

$$q = m\Delta H_{\text{trans}}$$

Entropy of a temperature change

$$\Delta S = mC_s \ln(T_f/T_i)$$

Entropy of a phase change

$$\Delta S = m\Delta H_{\text{trans}}/T$$

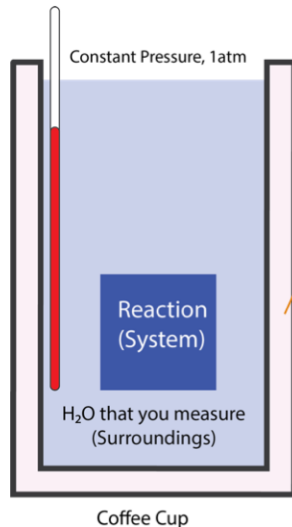
Coffee Cup Calorimetry, $q_p = \Delta H$

Coffee Cup: the goal here is to measure heat at constant pressure. This directly gives us the enthalpy (ΔH) for a reaction.

$$\rightarrow q_p = \Delta H$$
$$q_{\text{cal}} = m C_s \Delta T + C \Delta T$$

H₂O

$$q_{\text{cal}} = q_{\text{sur}} = -q_p$$



Insulated hardware does not absorb heat, so we don't care about the $C\Delta T$ term for the calorimeter

Bomb Calorimetry: $q_v = \Delta U$

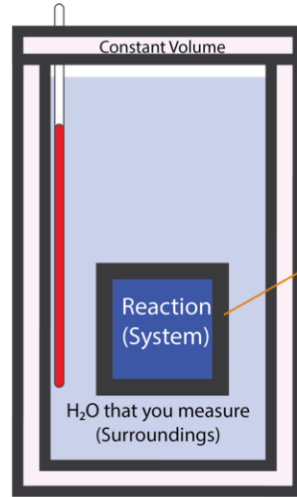
The goal is to get the internal energy change (ΔU) of a combustion reaction by measuring the ΔT of both the surrounding water and the hardware of the calorimeter

$$q = mC_s\Delta T + C\Delta T \rightarrow \frac{\text{kJ}}{^\circ\text{C}}$$

Handwritten notes:
- Under m : H_2O
- Under C : hardware
- Below m : $\rightarrow 4.000\text{L} \rightarrow 4,000\text{g}$

$$\text{kJ} = \text{kJ} + \text{kJ}$$

Handwritten notes:
- A red circle around the first kJ has an arrow pointing to "negative" and $\rightarrow q_{\text{cal}} = -q_{\text{sys}}$
- Below that: $\hookrightarrow \frac{\text{kJ}}{\text{mol}}$



Stainless steel hardware **does** absorb heat, so we **do** care about the $C\Delta T$ term for the calorimeter

Bomb Calorimeter

Rewriting the First Law

$$\Delta U_{\text{sys}} = q + w$$

$$\Delta U_{\text{sys}} = \Delta H - \Delta nRT \quad \checkmark$$

- if $w > 0$ ($\Delta n < 0$) $\Delta U > \Delta H$
- if $w < 0$ ($\Delta n > 0$) $\Delta U < \Delta H$

Enthalpy

ΔH = HEAT FLOW AT CONSTANT PRESSURE

Definition of Enthalpy

- **Enthalpy (H):** a state function that describes the heat content of a system, given by the equation:

$$H = U + PV$$

- However, in chemistry we are more concerned with the change in enthalpy, ΔH , which is simply the heat flow at constant pressure, q_p

$$\underline{\Delta H} = q_p$$

Hess' Law Calculations

Suppose you have a reaction but no way to directly calculate its enthalpy. You can “create” a path for your reaction using one of three techniques:

1. **The first technique is the one where you algebraically rearrange multiple steps that will equal the total enthalpy change of a single reaction**

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

2. **Formation reactions take the sum of the formation enthalpy of products minus the reactants**

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

3. **Bond dissociation enthalpy is the weird one that takes the bond strength of the reactants minus the products**

$$\Delta H_{rxn} = \sum BE(\text{react}) - \sum BE(\text{prod})$$

Hess' Law – Sum of Reactions

- **Goal: create your desired equation using a given set up hypothetical steps**

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots + \Delta H_n$$

- What you can do to “make” your sum of reactions equal your goal reaction: **multiply the entire reaction by a coefficient or fraction (including the enthalpy value associated with that step!)** or **reverse the entire reaction (changing the sign of the enthalpy value associated with that step).**
- I prefer going step-by-step to determine what adjustments need to be made (start at step one, make necessary adjustments, etc.)

Hess' Law – Formation Reactions

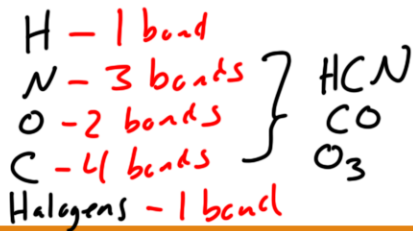
- Goal: determine the enthalpy of formation for your products and reactants. The enthalpy of the reaction is the difference between the products and reactants.

$$\Delta H_{rxn} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

Hess' Law – Bond Energy Data

- **Goal: determine the energy difference between all bonds breaking and all bonds forming**
- You must draw a proper Lewis structure, determine what kind of bonds are breaking (reactants) and what kind of bonds are forming (products), and take the difference.

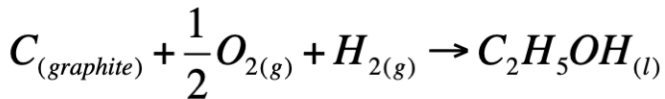
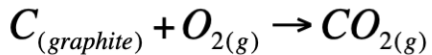
$$\Delta H_{rxn} = \sum^{Reactants} BE(react) - \sum^{Products} BE(prod)$$



When $\Delta H_f^\circ = \Delta H_{rxn}^\circ \longrightarrow 298K, 1atm$

Hess' Law – Formation Reactions

A formation reaction has one mole of one product formed by elements in their standard states.



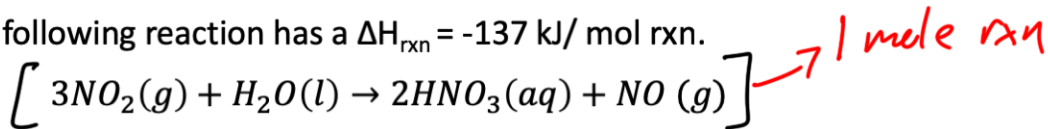
Phase and number of moles are important!

- 1) One Product
- 2) One mole Product
- 3) Formed from elements
in Std. state

↓
include
diatomics

Hess' Law Applied: Scaling Reaction Enthalpies

As written, the following reaction has a $\Delta H_{\text{rxn}} = -137 \text{ kJ/mol rxn}$.



1. What is ΔH per mole of NO_2 ?

$$-137 \frac{\text{kJ}}{\text{mol rxn}} \times \frac{1 \cancel{\text{mol rxn}}}{3 \text{ mol NO}_2} = -45.7 \frac{\text{kJ}}{\text{mol NO}_2}$$

2. What is ΔH for 13 g NO_2 ?

$$-45.7 \frac{\text{kJ}}{\text{mol NO}_2} \times \# \text{ of moles NO}_2 = 12.92 \text{ kJ} \rightarrow 13 \text{ g} \times \frac{\text{mol}}{46 \text{ g}} = 0.2826 \dots \text{ moles}$$

3. What is ΔH when 6 moles of NO_2 are reacted with 3 moles of H_2O ?

$$-137 \frac{\text{kJ}}{\text{mol rxn}} \times 2 \cancel{\text{mol rxn}} = -274 \text{ kJ}$$

$\hookrightarrow 2 \text{ mol rxn}$
 $\hookrightarrow 3 \text{ mol rxns}$
 $\hookrightarrow \text{extensive}$
 $\hookrightarrow \text{L.R.}$

Entropy

ENTROPY IS A MEASURE OF ENERGY DISPERSAL

Entropy is Energy Dispersal

In summation, you can increase entropy based on:

✓ 1. Phase (going from solid to liquid [to aqueous] to gas)

2. Increasing volume (decreasing pressure)

✓ 3. Increasing temperature

$$\Delta S = mC_s \ln \frac{T_f}{T_i}$$

} Macro

4. Complexity of your molecule (a larger number of more diverse bonds)

5. Complexity of your solution *we don't really talk about this

} Micro
} Statistical

6. Increasing the number of particles

The 2nd Law of Thermodynamics

- The second law of thermodynamics states that the entropy of the universe is always increasing.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

- This law gives us three conditions for ΔS_{total} :
 1. $\Delta S < 0$ (negative) ; your reaction is nonspontaneous
 2. $\Delta S = 0$ (zero) ; your reaction is at **equilibrium / reversible**
 3. $\Delta S > 0$ (positive) ; your reaction is spontaneous
- **Common mistake: you cannot make conclusions about ΔS_{sys} based on spontaneity alone**

Conceptual Entropy

Identify the sign of ΔS_{sys} for each process listed below:

1. A sample of water is cooled from 25°C to 12°C

(-)

2. A gas-phase reaction has a negative work value

(+)

$\overline{L} \rightarrow +\Delta n$

3. A fixed number of gas molecules expand to a slightly greater volume

(+)

4. The sublimation of carbon dioxide

(+)

5. CH_4 is halogenated to CH_3Cl (+)

Understand these
topics conceptually

Conceptual Entropy: Microview

- The relationship between entropy and microstates is given by the formulas:

$$\rightarrow S = k \ln \Omega \quad S = k \ln x^i$$

- Entropy depends on the **complexity of the molecule**, represented by the orientations possible (x)
 - Larger molecules with diverse sets of bonds are more complex (higher entropy)
- Entropy depends on the total number of particles, represented by " i "
 - Having more particles (or more moles) leads to a higher entropy

Ranking Molar Entropy

1) Phase $s \rightarrow l \rightarrow g$

2) Temperature

Complexity \rightarrow CH_4 vs CH_3Cl

CH_3OH vs $\text{CH}_3\text{CH}_2\text{OH}$

More bonds

diverse

S = J/K or J/mol K

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

Entropy: Quantifying Entropy

- Just like heat, change in entropy can be quantified with and without a temperature change.

- The trick to understanding how to quantify entropy is understanding the equations from which it is derived. **The key here is understanding the units of entropy: J/K**

- Entropy of a temperature change

$$q = mC_s \Delta T$$

If we integrate with respect to T to get entropy:

$$\Delta S = mC_s \ln \frac{T_f}{T_i}$$

- Entropy of a phase change

$$q = \Delta H_{trans}$$

If we divide by the temperature we get:

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} \rightarrow \neq T_{sys}$$

$\frac{J}{g \cdot ^\circ C} = \frac{J}{g \cdot K}$

Free Energy

A MEASUREMENT OF SPONTANEITY FOR A REACTION SYSTEM (-)

Defining Spontaneity

- **Spontaneous reactions happen without a continual input of energy.**
- **Non-spontaneous reactions don't happen unless you continually input energy.**
- There is an additional energy required (the activation energy) but we aren't worried about that just yet.

$$\Delta G_{\text{rxn}} < 0 \quad (-)$$
$$\Delta S_{\text{universe}} > 0 \quad (+)$$

- However, we can do non-spontaneous reactions in a variety of ways (inputting energy, electricity, reaction coupling, etc.); they just don't happen on their own.

Definition of Free Energy

- **Gibb's Free Energy (G):** A state function derived to describe the stability of a system. For now, we are concerned most with the ΔG because of the conclusions we can make using its **sign** and **magnitude**.
- The change in free energy of a reaction (ΔG) is the capacity for a system to do work. By running a spontaneous reaction, you are lowering the free energy of the universe (helping the universe along its path of inevitable demise).

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

KJ - T(KJ)

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

Remember: something inconvenient you might notice is that entropy is often provided in tables as J. Enthalpy is provided in tables as kJ. Make sure to adjust your units if you use the two state functions together!

Quantifying Chemical Change

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

KJ

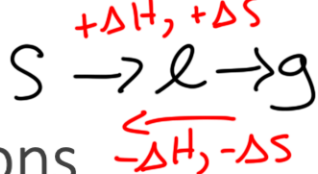
$$\sum n \Delta H_f^\circ, \text{products} - \sum n \Delta H_f^\circ, \text{reactants}$$

\downarrow

$\frac{J}{K} \rightarrow \frac{KJ}{K}$

$$\sum n S^\circ_{\text{products}} - \sum n S^\circ_{\text{reactants}}$$

Favorable:
 $+\Delta S, -\Delta H$



Spontaneity Conditions

A **negative free energy** is a spontaneous change

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

Requires energy
 $+\Delta H$
from surr.

Release energy
 \downarrow
T needs to be
small

$(-) = + - T(+)$ \rightarrow High T

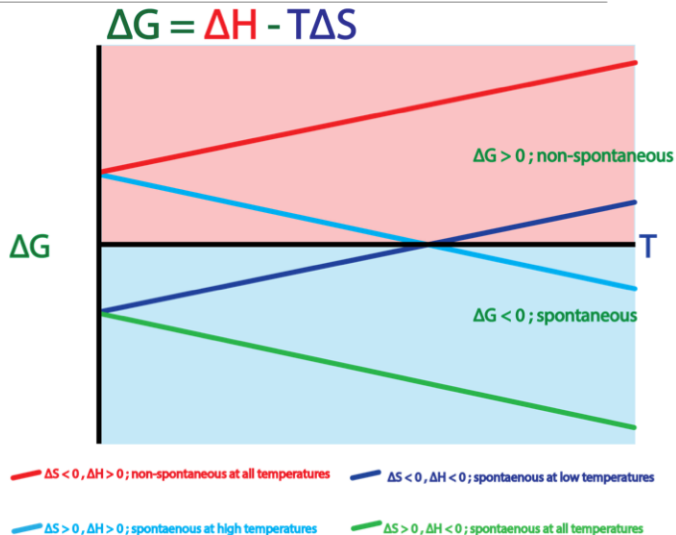
$(-) = - - T(-)$ \rightarrow Low T \leftarrow

$(-) = + - T(-)$ \rightarrow Never

$(-) = - - T(+)$ \rightarrow Always Spontaneous

Free Energy: All Conditions Summary

ΔH	ΔS	Temperature Dependent?	Spontaneous?
-	+	No	Always
+	-	No	Never
-	-	Yes	Low T
+	+	Yes	High T

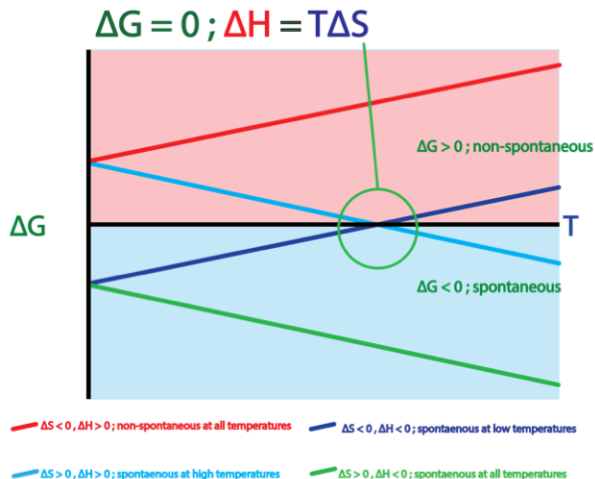


Free Energy: Equilibrium

For the conditions that are temperature dependent, it is possible to have a ΔG value equal to 0. This is, by definition, equilibrium.

In this class we are focused on one main equilibrium condition: phase change.

$$T_{trans} = \frac{\Delta H_{rxn}}{\Delta S_{rxn}}$$



Concept Check

What are the signs of ΔH , ΔS , and ΔG for the following processes?

1. Water freezing at 25°C

$$\Delta H (-) \quad \Delta S (-) \quad \Delta G (+)$$

2. Water melting at 12°C

$$+, +, -$$

3. Water vaporizing at 15°C

$$+, +, +$$

4. Water vaporizing at 115°C

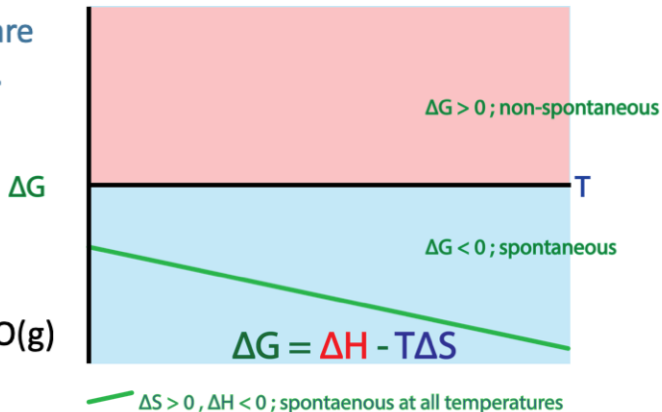
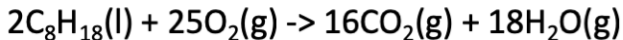
$$+, +, -$$

Free Energy: $-\Delta H$, $+\Delta S$

In this case, our enthalpy and entropy are “favorable” for a spontaneous reaction.

Therefore, this reaction will be **spontaneous** at all temperatures.

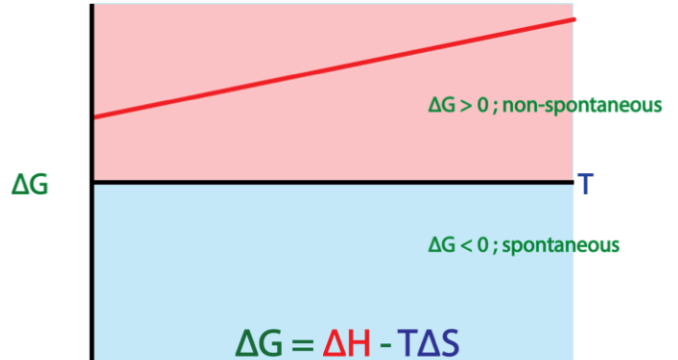
Example: many combustion reactions



Free Energy: $+\Delta H$, $-\Delta S$

In this case, our enthalpy and entropy are “unfavorable” for a spontaneous reaction.

Therefore, this reaction will be **nonspontaneous** at all temperatures.



$\Delta S < 0, \Delta H > 0$; non-spontaneous at all temperatures

Note on spontaneity: a positive ΔG does not mean that a reaction can't happen. It means that it doesn't happen without the continuous input of energy.

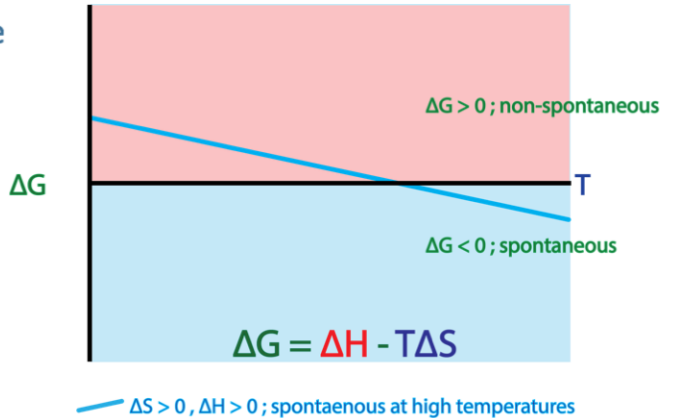
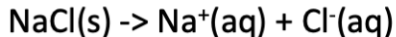
Free Energy: $+\Delta H$, $+\Delta S$

In this case, our enthalpy is unfavorable and our entropy is favorable.

This means that our $T\Delta S$ term must be greater in magnitude than our ΔH term in order for our ΔG to be negative.

In other words, our reaction is favored only at high enough temperatures.

Example: dissolution (favored at High T)



Free Energy: $-\Delta H$, $-\Delta S$

In this case, our entropy is unfavorable and our enthalpy is favorable.

This means that our $T\Delta S$ term must be smaller in magnitude than our ΔH term in order for our ΔG to be negative.

In other words, our reaction is favored only at low enough temperatures.

Example: cooling processes

