Chemistry

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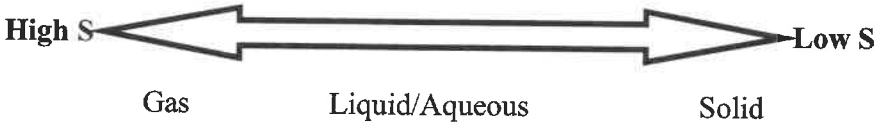
Name ____________________

ENTROPY

Entropy is a measure of the degree of disorder. (S or ΔS if talking about change)

The universe tends to move toward higher entropy (or in other words, reactions that increase entropy are favored.)
Solids have the lowest entropy, gases the highest. Liquids and aqueous ions are in between.



When chemical reactions move toward higher disorder, we say it is a positive ΔS. If it moves toward more order, we say it is a negative ΔS. If the type of phase does not make it clear how entropy is changing, you can also look at how many moles of each phase are present on each side of the reaction. For example, a reaction that goes from 1 mole of gas to 3 moles of gas would be an increase in entropy because there is more gas now (and more disorder).

Determine ΔS for the following reactions: (circle the appropriate answer)

1. $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$	Increase	Decrease
2. $H_2O_{(l)} \rightarrow H_2O_{(s)}$	Increase	Decrease
3. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$	Increase	Decrease
4. $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$	Increase	Decrease
5. $KCl_{(s)} \rightarrow KCl_{(l)}$	Increase	Decrease
6. $CO_{2(s)} \rightarrow CO_{2(g)}$	Increase	Decrease
7. $H^+_{(aq)} + CH_3COO^-_{(aq)} \rightarrow HCH_3COO_{(l)}$	Increase	Decrease
8. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	Increase	Decrease
9. $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$	Increase	Decrease
10. $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$	Increase	Decrease
11. $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$	Increase	Decrease
12. $2Al_{(s)} + 3I_{2(s)} \rightarrow 2AlI_{3(s)}$	Increase	Decrease
13. $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$	Increase	Decrease
14. $2NO_{(g)} \rightarrow N_{2(g)} + O_{2(g)}$	Increase	Decrease
15. $H_2O_{(g)} \rightarrow H_2O_{(l)}$	Increase	Decrease

Name ______________________________

GIBBS FREE ENERGY

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

T is temperature in Kelvins, ΔH is change in enthalpy or heat of reaction, ΔS is change in entropy

ΔG can be used to predict the spontaneity of a reaction:
$\Delta G > 0$ (+) means reaction **is not** spontaneous
$\Delta G < 0$ (-) means reaction **is** spontaneous
Note: Units for ΔH are usually kJ and units for ΔS are usually J, so you must fix that before cranking out any ΔG values!

Complete the table below for ΔG. You options are: always spontaneous, never spontaneous, spontaneous at high temperatures, spontaneous at low temperatures.

ΔH	ΔS	ΔG
-	+	
+	-	
-	-	
+	+	

Answer the questions below:

1. The conditions under which ΔG is always negative are when ΔH is ______________ and ΔS is ____________.

2. The conditions under which ΔG is always positive are when ΔH is ______________ and ΔS is ____________.

3. a) When you have an endothermic reaction that is going towards more disorder, high or low (circle one) temperature favors spontaneity.
   b) When you have an exothermic reaction that is going towards less disorder, high or low (circle one) temperature favors spontaneity.

Answer problems 4-6 with: always, sometimes, or never.
Note: If energy is on the reactants side, the reaction is endothermic. If energy is on the products side, the reaction is exothermic.

4. The reaction: $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ + energy will _____________ be spontaneous.

5. The reaction: energy + $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ will _____________ be spontaneous.

6. The reaction: energy + $H_2O_{(s)} \rightarrow H_2O_{(l)}$ will ______________ be spontaneous.

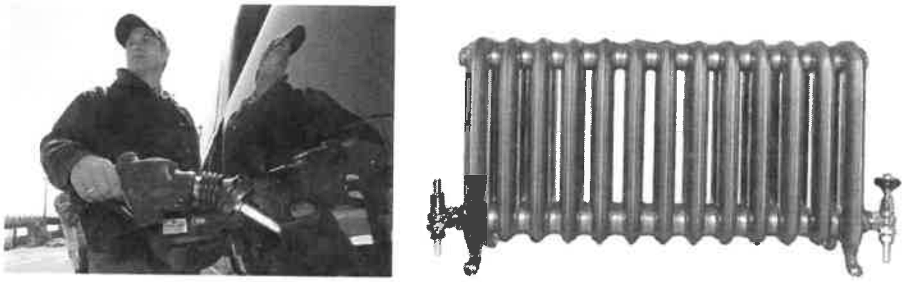
7. What is the value of ΔG if $\Delta H = -32.0$kJ, $\Delta S = +25.0$kJ/mol•K, and T=293K? ________________kJ

8. Is the reaction in problem 7 spontaneous? (circle one) yes no

9. What is the value of ΔG if $\Delta H = +12.0$kJ, $\Delta S = -5.00$kJ/mol•K, and T=290.K? ________________kJ

10. Is the reaction in problem 9 spontaneous? (circle one) yes no

Chemical Thermodynamics



Recall that, at constant pressure, the enthalpy change equals the heat transferred between the system and its surroundings.

$$\boxed{\Delta H = H_{final} - H_{initial} = q_p}$$

Thermodynamics involves enthalpy changes AND changes in order/disorder.

spontaneous processes: ones that occur without outside intervention

The First Law of Thermodynamics: Energy is conserved.

$$\Delta E = q + w$$

changes in system's internal energy

heat transferred

work done

If q is _−_, system released heat.

If q is _+_, system absorbed heat.

If w is _−_, system did work.

If w is _+_, system had work done on it.

Sign conventions are from system's point of view.

---

reversible process: "undo exactly what you did and you've got what you started with"

-- both system and surroundings go back to original states

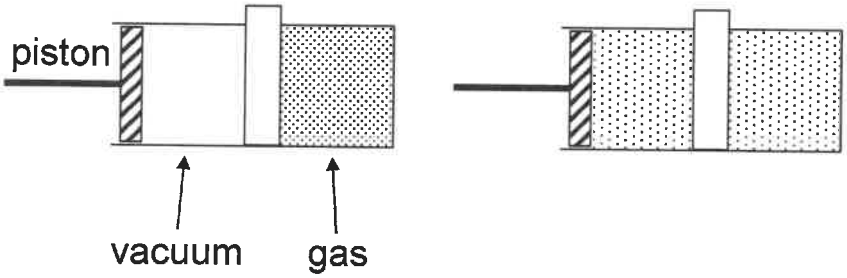
-- e.g., changes of state

ice @ 0°C $\underset{\text{take away X J}}{\overset{\text{add X J}}{\rightleftarrows}}$ water @ 0°C

irreversible process: getting back what you started with requires more than just an "undo"

-- we can restore the original system, but the surroundings will have changed

-- e.g., a gas expanding into an evacuated space



Points of note:

1. Whenever a chemical system is in equilibrium, we can go reversibly between reactants and products.
2. In any spontaneous process, the path between reactants and products is irreversible.
3. Thermodynamics refers to the direction of a reaction, not its speed.
4. In general, exothermic processes are more likely to be spontaneous.

Processes in which the system's disorder increases tend to occur spontaneously.

$\Delta S = S_f - S_i$

entropy, S

$+\Delta S$ → P are more disordered than R

$-\Delta S$ → P are more ORDERED than R

large entropy = large # of microstates = very disordered

small entropy = small # of microstates = less disordered

Entropy at the Particle Level

There are three types of motion, each having kinetic energy (KE).

-- translational, vibrational, rotational

-- The more KE we have, the more entropy we have. (i.e., the more microstates are possible)

In general… As T ↑/↓, S ↑/↓.

and… $S_{solid} < S_{liquid} < S_{gas}$

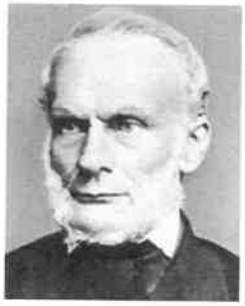
Process	freezing	melting	condensing	boiling
Sign of ΔS	−	+	−	+

The Second Law of Thermodynamics:

The entropy of an isolated system that is NOT in equilibrium will increase over time.

Sadi Carnot
(1796–1832)

The entropy of the universe increases in any spontaneous process.



Rudolf Clausius
(1822–1888)

Entropy is NOT conserved; it is constantly increasing.

For isolated systems… rev. → $\Delta S_{sys} = 0$

irrev. (i.e., spont.) → $\Delta S_{sys} > 0$

For a system in which heat is transferred at constant temperature…

$$\boxed{\Delta S = \frac{q}{T}}$$

-- T in K

-- common unit for entropy → J/K

i.e., $\frac{\text{heat (energy)}}{\text{temperature}}$

Find the change in entropy when 87.3 g of water vapor condense, given that water's heat of vaporization is 5.99 kJ/mol.

$$\Delta S = \frac{q}{T} = \frac{\underline{m}\,\Delta H_{vap}}{T} = \frac{87.3\,\cancel{g}\left(\frac{1\,\cancel{mol}}{18\,\cancel{g}}\right)\left(5.99\,\frac{kJ}{\cancel{mol}}\right)}{373.15\text{ K}}$$

$$= \boxed{-0.0779\ kJ/K} = \boxed{-77.9\ J/K}$$

Third Law of Thermodynamics:

The entropy of a pure, crystalline substance at absolute zero is…ZERO.

-- that would be a state of perfect order

(impossible)

Entropy increases when:

1. the number of gas particles increases

$$2\ NH_3 \rightleftharpoons \underbrace{N_2\ +\ 3\ H_2}_{\text{fewer bonds;}} \qquad +\Delta S$$

fewer restrictions on motion of atoms;
more degrees of freedom;
more possible microstates

2. liquids or solutions are formed from solids
3. gases are formed from liquids or solids

Which has the greater entropy?

1 mol $O_2(g)$ @ 300 K or 1 mol $O_2(g)$ @ 500 K
(same volume)

1 mol KCl(s) @ 300 K or 1 mol HCl(g) @ 300 K

2 mol HCl(g) @ 300 K or 4 mol HCl(g) @ 300 K
(same volume)

1 mol HCl(g) @ 300 K or 1 mol Ar(g) @ 300 K
(same volume)

2 mol HCl(g) @ 300 K (in a 10-L vessel) or 2 mol HCl(g) @ 300 K (in a 5-L vessel)

Calculating Entropy Changes

standard molar entropies, S°: molar entropy values of substances in their standard states

(i.e., pure substances at ~1 atm)

actually, at 1 bar = 10^5 Pa = 0.987 atm

S° values typically…

- are NOT zero
- ↑ w/increasing molar mass
- ↑ w/increasing # of atoms in formula

In a chemical reaction… $\boxed{\Delta S^\circ = \Sigma n S^\circ_P - \Sigma m S^\circ_R}$

(n and m are the coeff. for each substance)

Calculate the standard entropy change for…

$$P_4(s,\text{white}) + 10\,Cl_2(g) \rightarrow 4\,PCl_5(g)$$

177 223 353

tabulated values of S^o in J/mol-K

$\Delta S^o = \Sigma n S^o_P - \Sigma m S^o_R$

$\Delta S^o = 4(353) - [177 + 10(223)]$

$= \boxed{-995 \text{ J/K}}$

SMOKESCREEN OR FLESH-FRYER?

DANGER!

White phosphorus (or "WP") is used in bombs, artillery shells, and mortar shells that burst into burning flakes of phosphorus upon impact.

Gibbs Free Energy

Enthalpy changes (ΔH) and entropy changes (ΔS) both have a "say" in whether or not a rxn is spontaneous. Spontaneity is determined using the equation for Gibbs free energy…


Josiah Willard Gibbs
1839–1903

$$\boxed{\Delta G^{(o)} = \Delta H^{(o)} - T\Delta S^{(o)}}$$

$^{(o)}$ = std. conditions are optional

If $\Delta G < 0$… rxn. is spontaneous (i.e., as written)

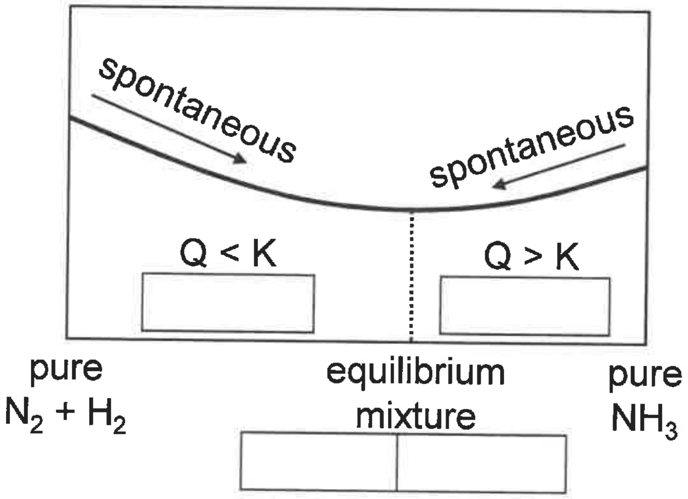
If $\Delta G > 0$… rxn. is nonspontaneous (i.e., spont. ←)

If $\Delta G = 0$… rxn. is AT equilibrium

(THIS INCLUDES PHASE CHANGES AT NBP OR NFP)

For the Haber process…

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$



standard free energies of formation, ΔG_f^o

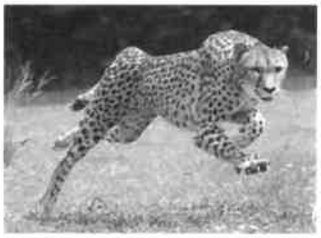
-- are tabulated for pure solids, pure liquids, gases at ~1 atm pressure, and 1 M solutions

-- For elements in their standard states… $\Delta G_f^o = 0$

-- For a reaction, the standard free-energy change is found by…

$$\boxed{\Delta G^o = \Sigma n G_f^o{}_P - \Sigma m G_f^o{}_R}$$

ΔG says WHICH WAY a reaction will proceed, but it says NOTHING about the reaction rate.



Calculate the standard free-energy change for…

$$PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$$

$PCl_3(g)$	$Cl_2(g)$	$PCl_5(g)$
–286.3	0	–324.6

tabulated ΔG_f^o's in kJ/mol

$$\Delta G^o = \Sigma n_p G_f^o{}_P - \Sigma n_r G_f^o{}_R$$

$$\Delta G^o = -324.6 - -286.3$$

$$= \boxed{-38.3 \text{ kJ}}$$

rxn. is spontaneous as written (i.e., left to right)

Free Energy and Temperature

From $\Delta G = \Delta H - T\Delta S$, we see that ΔG varies with temperature.

-- When T changes, so does ΔG.

-- ΔH and ΔS change little with temperature.

EX. (a) Calculate ΔH°, ΔG°, and ΔS° for…

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

ΔH_f° (kJ/mol)	90.3	0	33.2
ΔG_f° (kJ/mol)	86.7	0	51.8
S° (J/mol-K)	210.7	205	240

$\Delta H^\circ = 2(33.2) - [2(90.3)]$ $\boxed{\Delta H^\circ = -114.2\text{ kJ}}$

$\Delta G^\circ = 2(51.8) - [2(86.7)]$ $\boxed{\Delta G^\circ = -69.8\text{ kJ}}$

$\Delta S^\circ = 2(240.0) - [205.0 + 2(210.7)]$ $\boxed{\Delta S^\circ = -146.4\text{ J/K}}$

(b) Estimate ΔG at 400 K.

(Remember: ΔH and ΔS vary very, VERY little ^{w}/temp.)

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

$= -114{,}200\text{ J} - [400\text{ K}(-146.4\text{ J/K})]$

$= \boxed{-55{,}600\text{ J}}$

$= \boxed{-55.6\text{ kJ}}$

Estimate the normal boiling point of ethanol.

At the NBP… $CH_3CH_2OH(l) \rightleftharpoons CH_3CH_2OH(g)$

Strategy: Realize that $\Delta G = 0$.
Find ΔS and ΔH.
Solve for T in $\Delta G = \Delta H - T\Delta S$.

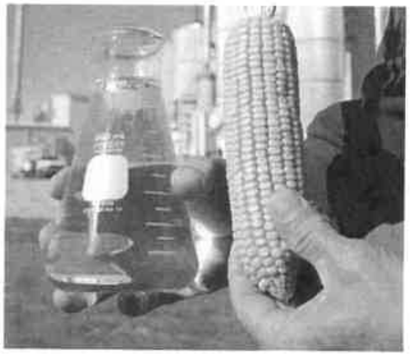
	L	**G**
S^o (J/mol-K)	160.7	282.7
ΔH_f^o (kJ/mol)	–277.7	–235.1

$\Delta S \cong \Delta S^o =$ 122 J/K $\Delta H \cong \Delta H^o =$ 42.6 kJ

From $\overset{0}{\cancel{\Delta G}} = \Delta H - T\Delta S$**…** $T = \dfrac{\Delta H}{\Delta S} = \dfrac{42{,}600 \text{ J}}{122 \text{ J/K}} = \boxed{349 \text{ K } (76^oC)}$

ΔH = 42,600 J; ΔS = 122 J/K

We estimated 76°C; the actual NBP of ethanol is 78.4°C.



From $\overset{0}{\cancel{\Delta G}} = \overset{+}{\Delta H} - \overset{351.4}{\cancel{T}}\overset{+}{\Delta S}$, we see that spontaneity (i.e., ΔG) depends on T.

Assume we start at 78.4°C, where $\Delta G = 0$…

As T increases, ΔG becomes
-- spontaneous, liquid to gas
As T decreases, ΔG becomes
-- spontaneous, gas to liquid

Free Energy and the Equilibrium Constant

ΔG^o is the standard free-energy change (i.e., for a reaction at standard conditions). Under **any other** conditions…

$$\boxed{\Delta G = \Delta G^o + RT \ln Q}$$

R = 8.314 J/mol-K

Q = rxn. quotient

Comparatively few reactions take place under standard conditions.

Calculate ΔG at 298 K, given the following:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

	$N_2(g)$	$3\,H_2(g)$	$2\,NH_3(g)$
(non-standard pressures)	1.0 atm	3.0 atm	0.50 atm
ΔG_f^o (kJ/mol)	0	0	–17

$\Delta G = \Delta G^o + RT \ln Q$

$\Delta G^o = 2(-17) = -34\text{ kJ} = -34{,}000\text{ J}$

$Q = \boxed{} = 0.00926$

$\Delta G = -34{,}000 + 8.314\,(298)\,(\ln 0.00926)$

$\boxed{\Delta G = -45.6\text{ kJ}}$

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

$$\boxed{\Delta G^{(o)} = -RT \ln K} \quad \text{and} \quad \boxed{K = e^{-\Delta G^{(o)}/RT}}$$

For gas-phase rxns, the K is K_p; for rxns. in soln, it is K_c.

Calculate ΔG° and K at 298 K for...

Assume all gases are at 1.00 atm of pressure.

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$

ΔG_f° (kJ/mol)	0	3.14	−53.22

$$\Delta G^\circ = 2(-53.22) - 3.14 = \boxed{-109.58\text{ kJ}}$$

$$K = e^{-\Delta G^\circ/RT} = e^{+109{,}580/(8.314)(298)} = \boxed{1.6 \times 10^{19}}$$

Rxn. is

What if we are relating/trying-to-find ΔG and/or K, but NOT at standard conditions?

-- To approx. K, given ΔG and nonstandard T:

Use $K = e^{-\Delta G/RT}$

-- To approx. ΔG, given K and nonstandard T:

Use $\Delta G = -RT \ln K$

-- To approx. K, given rxn eq and nonstandard T:

1. Use tabulated values to calc. ΔH° and ΔS°, which are "good" for all temps.
2. Use $\Delta G = \Delta H - T\Delta S$ and answers above to approx. ΔG at desired temp.
3. Use $K = e^{-\Delta G/RT}$ to approx. K at desired temp.

Gibb's Free Energy and Entropy Quiz

1. Which of the following would you expect to have the highest standard molar entropy? Explain.

a. CO_2 b. H_2O c. O_2 d. N_2

2. What would you expect the sign on ΔS be for a reaction that is known to be spontaneous? Explain.

3. A reaction has a $\Delta H = -356$ kJ/mol and $\Delta S = -36$ J/K. Calculate ΔG at 25° C and state if this reaction is spontaneous or nonspontaneous.

4. Calculate the standard free energy change for the following reaction.

$4\ KClO_3\ (s) + 3\ H_2S\ (aq) \rightarrow 4\ KCl\ (s) + 3\ H_2SO_4\ (aq)$

-304 -27.4 -408 -690

Gibb's Free Energy and Entropy Quiz

1. Which of the following would you expect to have the highest standard molar entropy? Explain.

a. CS_2 b. H_2S c. H_2 d. F_2

2. Explain why a reversible reaction at equilibrium would have a ΔS_{univ} of 0.

3. A reaction has a $\Delta H = -76$ kJ/mol and $\Delta S = 292$ J/K. Calculate ΔG at 298.15 K. Is the reaction spontaneous?

4. Calculate the standard free energy for the following reaction producing glucose.

$6\ CO_2\ (g) + 6\ H_2O\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6\ O_2\ (g)$

-394.4 -237 -911 0

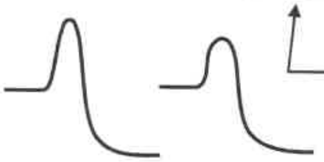
Factors that Govern Rates of Reactions

Generally...

(1) ...as the concentration of reactants increases, rate ↑

(2) ...as temperature increases, rate ↑

(3) ...with a catalyst, rate ↑



lowers activation energy and is NOT consumed (e.g., enzymes)

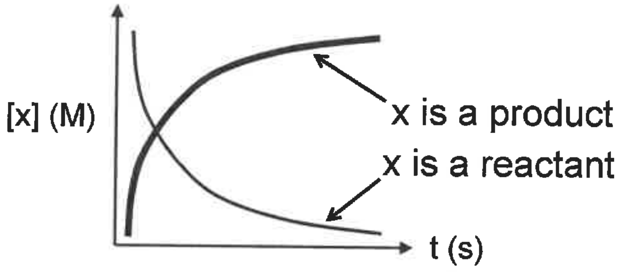
(4) ...as reactant surface area increases, rate ↑

Also, as mixing increases, rate increases.

Reaction rates are usually expressed in M/s.

$$\boxed{\text{rate} = \frac{\Delta[x]}{\Delta t}}$$

Conc. of Substance x v. Time



$\Delta[x]$ is (–) if x is a… reactant.

$\Delta[x]$ is (+) if x is a… product.

Coeff. in bal. eq. are used when comparing rates for substances in a rxn.

At a given time, the instantaneous rate of appearance of nitrogen dioxide is 3.2 x 10^{-6} M/s. Find the instantaneous rates of disappearance of nitrogen monoxide and oxygen at that time.

$$2\ NO(g) \quad + \quad O_2(g) \longrightarrow 2\ NO_2(g)$$

-3.2×10^{-6} M/s	-1.6×10^{-6} M/s	$+3.2 \times 10^{-6}$ M/s

Generally, reaction rates are proportional to the [ ] of reactants.

rate law: an expression that shows how the rate depends on the [ ]s of reactants

-- contains a rate constant, k

-- A rate law has the form... $\boxed{\text{rate} = k\ [R_1]^m\ [R_2]^n\ldots}$

where m and n are... reaction orders

(Their sum is the overall reaction order; r.o.'s are determined experimentally.)

-- Usually, reaction orders are 0, 1, or 2, but some are fractions or are (–).

If a reaction is zero order in a particular reactant, changing its concentration...does NOT affect the rate, as long as there is SOME of the reactant present.

1st order: ∝ changes

(double the [ ],

(halve the [ ],

2nd order: squared changes

(triple the [ ],

(halve the [ ],

The rate constant k is NOT affected by concentration, but it **IS** affected by... temperature and catalysts.

$H_2(g) + Cl_2(g) \longrightarrow 2\ HCl(g)$

Find...

(1) rxn order of each reactant

(2) overall reaction order

(3) units of rate constant

	$[H_2]$ (M)	**$[Cl_2]$ (M)**	**Init. rate of HCl formation (M s^{-1})**
A	0.100	0.100	0.340
B	0.100	0.200	0.680
C	0.200	0.200	2.720

r.o. of H_2 = 2
r.o. of Cl_2 = 1

o.r.o. = 3

rate = $k\,[H_2]^2\,[Cl_2]$

$\frac{M}{s} = ?\ \ M^2\ \ \ M$

units for k = $\frac{1}{M^2 \bullet s} = M^{-2}\ s^{-1}$

Rate laws can be converted into equations that give the concentrations of substances at any time during the course of a reaction.

First-Order Reactions

-- Rate laws for 1st order rxns have the form:

$$\text{rate} = k\,[A]$$

You can use P instead of [A] in rate law equations (if you have a gaseous system).

-- To find rxn [ ]s over time, use…

$$\ln [A]_t = \ln [A]_o - kt \quad \text{or…} \quad \boxed{kt = \ln \frac{[A]_o}{[A]_t}}$$

Plotting ln $[A]_t$ v. t gives a straight line w/slope…

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

If this is a first-order process, with $k = 6.8 \times 10^{-4}\ s^{-1}$ and w/the initial pressure of $(CH_3)_2O$ being 256 torr, find the partial pressure of $(CH_3)_2O$ after 36.5 min.

For gases, P ∝ mol (and therefore [ ]), so…

$$kt = \ln \frac{[A]_o}{[A]_t} \quad \text{becomes} \quad kt = \ln \frac{P_o}{P_t}$$

$$6.8 \times 10^{-4}\ s^{-1}\ (2190\ s) = \ln (256/P_t)$$

$$1.4892 = \ln (256/P_t)$$

Taking "e-to-the-both-sides" yields…

$$4.4335 = 256/P_t$$

$$\boxed{P_t = 57.7\ \text{torr}}$$

Half-life of a reaction, $t_{1/2}$: the time required for a reactant's [ ] to drop to ½ of its orig. value

For 1st order rxns: $\boxed{k\,t_{1/2} = 0.693 = \ln 2}$

[redacted]

Ernest Rutherford is given credit for discovering the concept of radioactive half-life. It was later shown that the same math applies to the kinetics of first-order chemical reactions.

Second-Order Reactions (that are 2nd order in just one reactant)

e.g.,

$$\boxed{kt = \frac{1}{[A]_t} - \frac{1}{[A]_o}} \quad \text{and} \quad \boxed{k\,t_{1/2} = \frac{1}{[A]_o}}$$

($t_{1/2}$ DOES depend on init. [ ] of reactant A... AND $t_{1/2}$ changes w/time. (!))

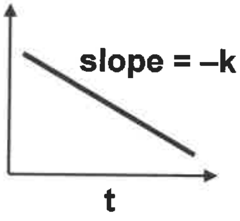
Plotting $\frac{1}{[A]_t}$ v. t gives a straight line w/slope...

** Above equations do NOT apply to 2nd order reactions that are 1st order in two reactants.

1^{st} order rxns

$$k\,t_{1/2} = 0.693 = \ln 2$$

$$kt = \ln\frac{[A]_o}{[A]_t}$$

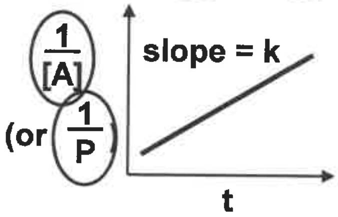


"It's natural to want to finish 1^{st}."

2^{nd}-order-in-only-one-R rxns

$$k\,t_{1/2} = \frac{1}{[A]_o}$$

$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_o}$$



"To **want** to finish 2^{nd}? That's upside-down thinking."

Rate Laws WS

1. The rate of the reaction $O_{(g)} + NO_{2(g)} \rightarrow NO_{(g)} + O_{2(g)}$ was studied at a certain temperature.
   (a) In the first set of experiments, NO_2 was in large excess, at a concentration of 1.0×10^{13} molecules/cm^3 with the following data collected:

Time (s)	**[O] (atoms/cm^3)**
0	5.0×10^9
1.0×10^{-2}	1.9×10^9
2.0×10^{-2}	6.8×10^8
3.0×10^{-2}	2.5×10^8

   What is the order of the reaction with respect to oxygen atoms?

   (b) The reaction is known to be first order with respect to NO_2. Determine the overall rate law and the value of the rate constant.

2. The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1}. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm^3.
   (a) What is the concentration of the insecticide on June 1 of the following year?

   (b) How long will it take for the concentration of the insecticide to decrease to 3.0×10^{-7} g/cm^3?

3. The decomposition of dimethyl ether, $(CH_3)_2O$ at 510° C is a first-order process with a rate constant of 6.8×10^{-4} s^{-1}.

$$(CH_3)_2O_{(g)} \rightarrow CH_{4(g)} + H_{2(g)} + CO_{(g)}$$

   If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its pressure after 1420 s?

4. Consider a hypothetical reaction:

$$A + B \longrightarrow C$$

Experiment	[A] (mol/L)	[B] (mol/L)	Rate (mol·L^{-1}/s x 10^{-5})
1	0.100	0.100	4.0
2	0.100	0.200	4.0
3	0.200	0.100	16.0

a) Determine the rate law expression for this reaction.
b) What is the order of reaction with respect to A? to B?
c) What is the overall reaction order?

5. In a reaction involving only one reactant, A, the rate of the reaction increases by a factor of 27 when the concentration of A is tripled. What is the rate law expression for this reaction?

6. $A + B \longrightarrow C + D$ $r = k[A]^2[B]^2$
The rate of the reaction is 1.0 x 10^{-4} M/s when the concentration of A is 0.40 M and the concentration of B is 0.30 M. Calculate the, rate of the reaction when the concentration of A is 0.85 M and the concentration of B is 0.75 M.

7. $A + B \longrightarrow C$ $r = k[A]^2[B]^0$
The rate of the reaction is 4.0 x 10^{-5} M/s when the concentration of A is 0.100 M. Calculate the rate of the reaction when the concentration of A is 0.550 M.

8. $2HI \longrightarrow H_2 + I_2$ $r = k[HI]^2$
The rate of reaction is 2.5 x 10^{-4} M/s when the concentration of HI is 0.0588 M. Calculate the new rate of reaction if the concentration of HI is 0.0885 M.

9. The decomposition of N_2O_5 has the rate law: $r = k[N_2O_5]$.
If k = 1.0 x 10^{-5} 1/s, what is the rate of the reaction when the concentration of N_2O_5 is 0.0010 M?

Thermodynamics Review

What is the sign of the change in entropy for each process?

1A. melting

subliming

freezing

1B. mixing two components of a mixture

separating a mixture's components

boiling

Which species has the greater entropy?

2A. 1 mol N_2 at STP or 1 mol N_2 at 200°C, 0.25 atm

1 mol $H_2O(l)$ at 100°C or 1 mol $H_2O(g)$ at 100°C

2B. 1 mol O_2 at STP or 1 mol O_2 at 50 K, 3.0 atm

1 mol $CH_4(g)$ at 0°C or 1 mol $H_2O(l)$ at 75°C

Predict the sign of the standard entropy change for each reaction. Then use tabulated values to calculate ΔS°.

3A. $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$

3B. $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

At what temperature range, if any, will each process be spontaneous?

4A. $\Delta H = -21$ kJ, $\Delta S = -70.$ J/K

4C. $\Delta H = +21$ kJ, $\Delta S = -70.$ J/K

4B. $\Delta H = -21$ kJ, $\Delta S = +70.$ J/K

4D. $\Delta H = +21$ kJ, $\Delta S = +70.$ J/K

5A. For the reaction $2\ NO(g) + O_2(g) \leftrightarrow N_2O_4(g)$ $\Delta H^\circ = -170.6$ kJ and $\Delta S^\circ = -322.4$ J/K. Use tabulated values to find ΔG°. Then find the Celsius temperature at which $\Delta G = 0$. Finally, state the temperature range over which the reaction is spontaneous <u>and</u> the temperature range over which it is NOT spontaneous.

6A. Given the following: $2\,H_2(g) + C(s) \rightarrow CH_4(g)$ $\Delta G^\circ = -51$ kJ
$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$ $\Delta G^\circ = -474$ kJ
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^\circ = -394$ kJ

Determine ΔG° for $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$.

6B. Given the following: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^\circ = -394$ kJ
$H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(l)$ $\Delta G^\circ = -237$ kJ
$2\,C_6H_6(l) + 15\,O_2(g) \rightarrow 12\,CO_2(g) + 6\,H_2O(l)$ $\Delta G^\circ = -6399$ kJ

Determine ΔG° for $6\,C(s) + 3\,H_2(g) \rightarrow C_6H_6(l)$.

Substance and State	**ΔH_f° (kJ/mol)**	**ΔG_f° (kJ/mol)**	**S° (J/mol-K)**
$Br_2(g)$	31	3.14	245
$Br_2(l)$	0	0	152
$CO_2(g)$	−393.5	−394	214
$C_3H_8(g)$	−104	−24	270.
$C_6H_{12}O_6(s)$	−1275	−911	212
$Cl_2(g)$	0	0	223
$CH_3CH_2OH(g)$	−235.1	−168	282.7
$CH_3CH_2OH(l)$	−277.7	−175	160.7
$HBr(g)$	−36	−53	199
$HCl(g)$	−92	−95	187
$H_2(g)$	0	0	131
$H_2O(l)$	−286	−237	70.
$H_2O(g)$	−242	−229	189
$H_2S(g)$	−21	−34	206
$NH_3(g)$	−46	−17	193
$NO(g)$	90.3	86.7	210.7
$NO_2(g)$	33.2	51.8	240.
$N_2O_4(g)$	10.	98	304
$O_2(g)$	0	0	205
$O_3(g)$	143	163	239
$P_4(s)$	0	0	177
$PCl_3(g)$	−270.	−286.3	312
$PCl_3(l)$	−272	−320	217
$PCl_5(g)$	−278	−324.6	353
$S(s)$	0	0	32
$SO_2(g)$	−297	−300.	248
$SO_3(g)$	−396	−371	257

Thermodynamics Test

Part 1: Multiple Choice (/16pts)

1. Which of the following processes has negative entropy?

a. evaporating 1 mol of a liquid
b. heating 1L of water from 295K to 350K
c. freezing 1 mol of a liquid
d. none of the above

2. Which of the following conditions favor a spontaneous reaction at any temperature?

a. positive ΔH; positive ΔS
b. positive ΔH; negative ΔS
c. negative ΔH; positive ΔS
d. negative ΔH; negative ΔS

3. In an exothermic reaction the enthalpy change is __________, because energy is ___________.

a. negative; absorbed
b. positive; released
c. negative; released
d. positive; absorbed

4. What are the units for ΔG^o ?

a. J/K·mol
b. kJ
c. kJ/mol
d. J/g·K

5. Two metals with equal mass but different specific heats absorb the same amount of heat. Which metal undergoes the smaller change in temperature?

a. the metal with the higher specific heat
b. the metal with the lower specific heat
c. both undergo the same change in temperature
d. cannot be determined

6. How much energy would be absorbed as heat by 50. grams of Ethanol (C_p= 2.44 J/g·K) when heated from 253K to 276K?

a. 1800 J
b. 2800 J
c. 34,000 J
d. 31,000 J

7. If 250 J of work is done on the system and 25 J of heat is released by the system as a result, what is the internal energy of the system?

a. 280 J
b. -280 J
c. 225 J
d. -225 J

8. 22.5 g of a substance absorbs 625 J of energy and its temperature rises from 25.0° C to 32.3° C as a result. Determine the specific heat capacity of this substance.

a. 105 J/g·°C
b. 1.11 J/g·°C
c. 3.81 J/g·°C
d. 64.3 J/g·°C

Part 2: Short Answer (/16 pts)

1. What does it mean for a process to be reversible or irreversible? Provide an example of each.

2. Describe three ways in which the entropy of a system could be increased. Provide examples to justify your responses.

3. Calculate the ΔG° for the reaction of $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$. ΔH°= -395.5 kJ/mol ΔS°= 214 J/mol·K

4. Calculate the enthalpy for the following reaction:

$2C_{(s)} + H_{2(g)} \rightarrow C_2H_{2(g)}$ ΔH= ???

Given the following thermochemical equations:

$C_2H_{2(g)} + 5/2\ O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(l)}$ ΔH= -1299.5 kJ

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ΔH= -393.5 kJ

$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ ΔH= -285.8 kJ

Part 3: Free Response (/15pts)

$2\ Fe(s) + \frac{3}{2}\ O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H_f^\circ = -824$ kJ/mol

Iron reacts with oxygen to produce iron(III) oxide as represented above. A 75.0 g sample of $Fe_{(s)}$ is mixed with excess $O_{2(g)}$ at 298 K.

(a) Calculate the number of moles of Fe_2O_3 produced when the reaction proceeds to completion.

(b) If the above reaction is carried out in a bomb calorimeter filled with 10.0 L of water, what will the change in the temperature of the water be? ($c_{p,l}$ of H_2O = 4.18 J/g·K)

(c) The standard free energy of formation, ΔG_f° of Fe_2O_3 is –740. kJ/mol at 298 K.

(i) Calculate the standard entropy of formation ΔS_f° of Fe_2O_3 at 298 K. Include units with your answer.

(ii) Which is more responsible for the spontaneity of the formation reaction at 298K, the standard enthalpy or the standard entropy?