

MONDAY, APRIL 6, 2026 APCHEMISTRY

## CH. 19 THERMODYNAMICS

SPONTANEOUS = THERMODYNAMICALLY FAVORABLE, AS IN, HIGH IN POTENTIAL ENERGY. NOT NECESSARILY GUARANTEED TO HAPPEN.

SOME EVENTS ARE SPONTANEOUS, THAT IS, THEY HAPPEN ON THEIR OWN GIVEN CERTAIN CIRCUMSTANCES. FOR EXAMPLE, HOT COFFEE COOLS OFF, A DROPPED GLASS SHATTERS.

SOME EVENTS ARE NON-SPONTANEOUS AND EITHER NEVER HAPPEN (A SHATTERED GLASS REASSEMBLES) OR ONLY HAPPEN IF CIRCUMSTANCES CHANGE (ICE MELTS IF YOU ADD HEAT BUT STAYS SOLID BELOW  $0^{\circ}\text{C}$ ).

WE CAN DECIDE WHETHER A CHEMICAL RXN, FOR EX., IS SPONTANEOUS (A TECHNICAL TERM) ON THE BASIS OF THE ASSOCIATED CHANGE IN ENTROPY OF THE SYSTEM AND ITS SURROUNDINGS. (WE'LL DEFINE ENTROPY IN A MOMENT). SPECIFICALLY, WHEN THE TOTAL ENTROPY OF THE UNIVERSE INCREASES IN A PROCESS THEN IT IS SPONTANEOUS.

ENTROPY IS QUANTIFIED IGNORANCE. IT IS LITERALLY IMPOSSIBLE TO KNOW THE LOCATION ( $x, y, z$  COORD.) AND VELOCITY OF EVERY PARTICLE IN A SAMPLE OF GAS.

IN FACT, MANY VARIATIONS ON THE POSITIONS AND VELOCITIES OF PARTICLES ARE POSSIBLE FOR THE SAME VOLUME ( $V$ ), PRESSURE ( $P$ ), NUMBER OF MOLES ( $n$ ), AND TEMP. ( $T$ ).

ENTROPY ACCOUNTS FOR THIS IGNORANCE BY COUNTING (THEORETICALLY, AT LEAST) THE NUMBER OF WAYS ( $W$ ) THE MOLECULES CAN BE ARRANGED (AS TO POSITION AND VELOCITY, ETC.) WITHOUT ALTERING  $V$ ,  $P$ ,  $n$ , OR  $T$ :

ENTROPY USES THE VARIABLE  $S$

$k$  IS THE BOLZMANN CONSTANT  $k = 1.38 \times 10^{-23} \text{ J/K}$

$$S = k \cdot \ln(W)$$

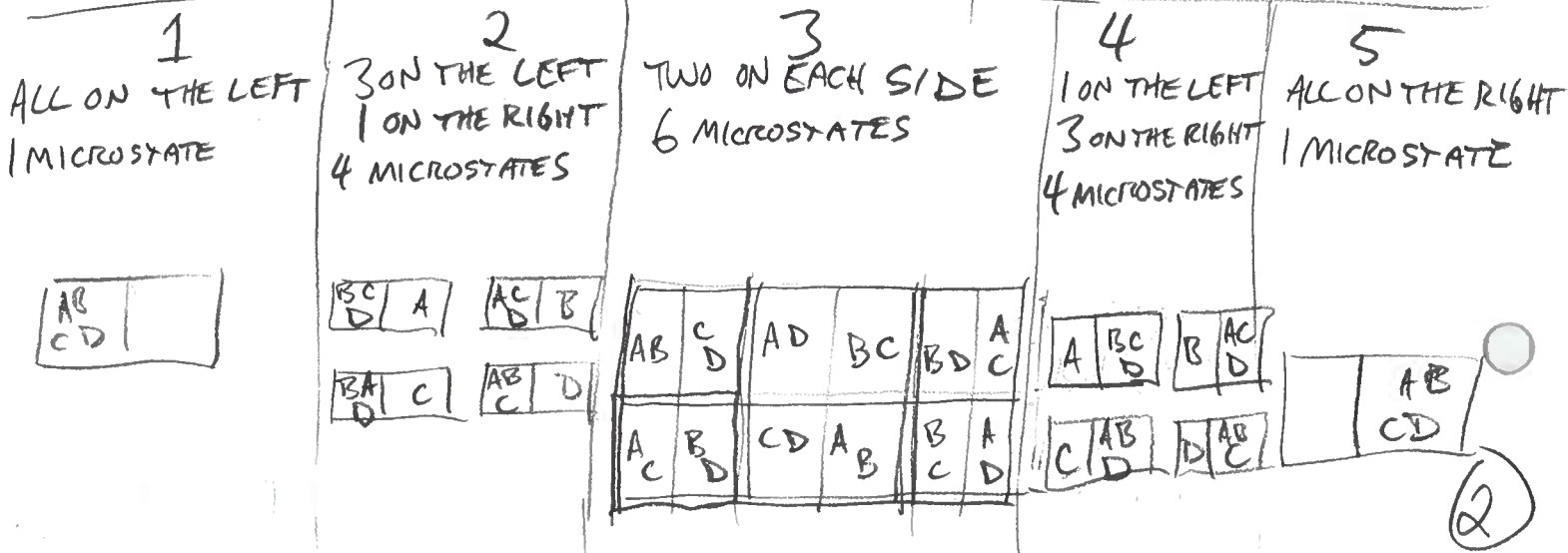
FROM APPENDIX C

FOR 1 mol OF  $N_2$  AT 298K THE STANDARD ENTROPY ( $S^\circ$ ) IS 192 J/K. ACCORDING TO THE EQUATION ABOVE THIS MEANS

THERE ARE:  $W = e^{S/k} = e^{\frac{192 \text{ J/K}}{1.38 \times 10^{-23} \text{ J/K}}} = e^{1.4 \times 10^{25}}$

WHICH IS ABOUT  $10^{6 \times 10^{24}}$  WAYS TO ARRANGE THE  $N_2$  MOLECULES.

AS THIS IS A BIT HARD TO GRASP, LET'S LOOK AT A SIMPLER SITUATION: FOUR PARTICLES (A, B, C AND D) IN TWO CONNECTED BOXES. THE ENTROPY CAN BE THOUGHT OF AS THE NUMBER OF INDISTINGUISHABLE MICROSTATES FOR A GIVEN MACROSTATE; THERE ARE FIVE MACROSTATES.



M 2026-04-06 AP CHEM

THE MEASURE OF ENTROPY IS THE NUMBER OF MICROSTATES WHICH MAKE AN EQUIVALENT MACROSTATE. TAKE MACROSTATE 3 IN THE SCENARIO AT THE BOTTOM OF THE PREV. PG.

TWO PARTICLES IN EACH OF TWO BOXES CAN HAPPEN A TOTAL OF SIX WAYS. MACROSTATES 1 AND 5 EACH HAVE ONLY ONE MICROSTATE. MACROSTATE 3 HAS THE MAXIMUM ENTROPY IN THIS SCENARIO. AND IF THE PARTICLES MOVE FREELY BETWEEN THE BOXES IT IS ALSO THE MOST PROBABLE STATE: SIX OUT OF SIXTEEN TOTAL MICROSTATES HAVE 2 PARTICLES IN EACH BOX.

AND SO WE SEE THE CONNECTION BETWEEN ENTROPY AND PROBABILITY. THE REASON WHY SYSTEMS TEND TOWARD MAXIMUM ENTROPY IS SIMPLY BECAUSE THE STATE WITH THE HIGHEST ENTROPY IS THE MOST PROBABLE.

REMEMBER, PARTICLES ARE IN CONSTANT RANDOM MOTION. AS A RESULT, PARTICLES IN A SYSTEM "EXPLORE" THE PHASE SPACE, OR ALL THE DIFF. DISTRIBUTIONS OF POSITION, VELOCITY, AND ENERGY. THEY QUICKLY MOVE TO THE MOST PROBABLE, OR HIGHEST ENTROPY, STATE BECAUSE THEY ARE ALL MOVING SO FAST.

SO THIS IS WHY SOLIDS DISSOLVE: THERE ARE MANY, MANY MORE POSITIONS AVAIL. TO PARTICLES IN THE SOLVENT THAN WHEN THEY ARE CONFINED IN A CRYSTAL.

THIS IS WHY THE SMELL OF FRESH COOKIES SPREADS ACROSS THE ROOM: THE SCENT MOLECULES FREELY MOVE AND SO IT'S MORE PROBABLE FOR THEM TO DISPERSE THAN TO STAY PUT.

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# MACROSCOPIC DEFINITION OF ENTROPY

IT'S IMPRACTICAL TO CALC VALUES OF ENTROPY ( $S$ ) USING  $S = k \cdot \ln(W)$  B/C IT'S IMPOSSIBLE TO ACTUALLY COUNT THE WAYS PARTICLES CAN BE ARRANGED.

INSTEAD, WE USE THIS DEFINITION OF THE CHANGE IN ENTROPY OF THE SYSTEM ( $\Delta S_{\text{sys}}$ ) OR SURROUNDINGS ( $\Delta S_{\text{sur}}$ ).

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

WHERE  $q$  IS HEAT TRANSFERRED AT CONSTANT TEMP. (K)

$\Delta S$  IS A STATE FUNCTION:  $\Delta S = S_f - S_i$

UNLIKE  $\Delta H$ , WHICH CAN ONLY BE GIVEN AS A CHANGE, ABSOLUTE VALUES, OR STANDARD ENTROPIES ( $S^\circ$ ) ARE TABULATED FOR VARIOUS MATERIALS AT STANDARD TEMP. AND PRESSURE (1 atm AND 298 K).  
AND 1 mol/L

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## THE LAWS OF THERMODYNAMICS

FIRST LAW: ENERGY IS NEITHER CREATED NOR DESTROYED.

OR

THE ENERGY CONTENT OF THE UNIVERSE IS CONSTANT.

OR

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

SECOND LAW: PER LORD KELVIN: "NO PROCESS IS POSSIBLE IN WHICH THE SOLE RESULT IS THE ABSORPTION OF HEAT FROM A RESERVOIR AND ITS COMPLETE CONVERSION TO WORK."

OR

IN ANY REAL PROCESS EITHER THE ENTROPY OF THE SYSTEM OR THE SURROUNDINGS (OR BOTH) INCREASES. THE ENTROPY OF THE UNIVERSE ALWAYS INCREASES.

OR

FOR A PROCESS TO BE SPONTANEOUS THE ENTROPY OF THE UNIVERSE MUST INCREASE

$$\Delta S_{\text{univ}}^{\text{OR}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

THIRD LAW: (THIS ONE IS A BIT NICHE)

THE ENTROPY OF A PERFECT CRYSTAL AT ABSOLUTE ZERO (0K) IS ZERO. THIS IS B/C THERE IS ONLY ONE WAY TO ARRANGE PARTICLES:  $S = k \cdot \ln(W)$  AND  $k \ln(1) = 0$ . (WE NEEDED THIS LAW TO BE ABLE TO TABULATE STANDARD ENTROPIES,  $S^\circ$ ).

YOUR TEXTBOOK COVERS A BIT OF THE HISTORY OF THE DEVELOPMENT OF THERMODYNAMICS, WHICH GOES BACK ABOUT 200 YEARS. AT THAT TIME STEAM ENGINES WERE NEW AND PHYSICISTS AND ENGINEERS WERE INTERESTED IN OBTAINING THE MAXIMUM AMOUNT OF WORK FOR A GIVEN AMOUNT OF COAL BURNED. (HEAT IS TURNED INTO WORK, FOR EX., BY USING A FIRE TO HEAT A GAS SO IT EXPANDS IN A PISTON, WHICH MAKES A WHEEL TURN) \* SEE ALSO THE STIRLING ENGINE DEMO USING HOT WATER AND ICE.

THEY FOUND THAT THEY COULD ACHIEVE A CONVERSION OF HEAT INTO WORK OF 5-10% (LET'S SAY). MODERN GASOLINE-POWERED CARS ARE 20-40% EFFICIENT.

SO IF THE ~~FIRST~~ FIRST LAW IS TRUE, WHERE DID THE REST OF THE ENERGY GO? THE SHORT ANSWER IS THAT THE HEAT ENERGY NOT TURNED INTO WORK INSTEAD INCREASED ENTROPY.

IN PRACTICAL TERMS, THE INCR. IN ENTROPY IS SEEN IN HOW THE UNIFORMLY MOVING PISTON INCREASES THE RANDOM MOTION OF GAS MOLECULES INSIDE IT. OR, IN HOW HEAT MAKES THE ENGINE, AND THE SURROUNDINGS HOTTER. OR, IN HOW A MACHINE PROPELLED BY THE ENGINE SLOWS TO A HALT, ITS ENERGY OF MOTION BECOMING HEAT.

THE BOOK DISCUSSES AN IDEAL, REVERSIBLE ENGINE. THIS IS A THOUGHT EXPERIMENT WHICH IS MEANT TO ILLUSTRATE HOW HEAT IS A DIFFERENT CONCEPT FROM ENTROPY. IT MANAGES THIS AS FOLLOWS: IN ORDER TO OPERATE AN ENGINE WITHOUT INCREASING ENTROPY IT MUST WORK IN THE FOLLOWING WAY. IT MUST OPERATE ISOTHERMALLY (OR WITHOUT CHANGING TEMPERATURE). IT MUST MOVE ONLY IN INFINITESIMALLY SMALL STEPS SO THAT IT ALWAYS REMAINS AT EQUILIBRIUM. SO IF AN ENGINE CHANGES TEMP. OR OPERATES WITH NORMAL MOTIONS IT WILL CAUSE ENTROPY TO INCREASE, WHICH SAPS THE ENGINE'S EFFICIENCY. AND SO WE DEMONSTRATE THE NECESSITY THAT NO REAL PROCESS CAN OCCUR WHICH DOES NOT ALSO INCREASE ENTROPY. THAT IS, WE DEMONSTRATE THE SECOND LAW.

A PRACTICAL MATTER: IT IS OFTEN USEFUL TO KNOW THE STANDARD CHANGE IN ENTROPY ( $\Delta S^\circ$ ) FOR A CHEMICAL REACTION. THIS IS  $\Delta S$  FOR THE (IDEALIZED) CIRCUMSTANCES IN WHICH WE TAKE REACTANTS UNDER STANDARD CONDITIONS AND CORRECT CONDITIONS FOR PRODUCTS BACK TO STD CONDITIONS ( $P=1\text{atm}$   $T=298\text{K}$   $[X]=1\text{M}$ ).

STANDARD ENTROPY VALUES ( $S^\circ$ ) ARE TABULATED IN APPENDIX C.

THINGS TO NOTE:

- ① UNITS ARE  $\text{J/K}$  (OR  $\text{J/K}\cdot\text{mol}$ ) (FOR REAL, NOT KIDDING!)
- ②  $S^\circ$  IS NEVER ZERO, EVEN FOR ELEMENTS

( $\Delta H_f^\circ$  IS ZERO, YOU MAY REMEMBER, FOR ELEMENTS B/C IT IS THE ENTHALPY CHANGE TO FORM AN ELEMENT FROM ITSELF.)

- ③ ENTROPY VALUES TRACK WITH PHASE OF MATTER:

$$S^\circ_{\text{GAS}} \gg S^\circ_{\text{LIQ.}} > S^\circ_{\text{SOL.}}$$

- ④ SUBSTANCES WITH A HIGHER MOLAR MASS AND/OR A LARGER NO. OF ATOMS WILL HAVE A LARGER  $S^\circ$ .

USE THIS FORMULA FOR  $\Delta S^\circ_{\text{RXN}}$ :

$$\Delta S^\circ_{\text{RXN}} = \sum n S^\circ_{(\text{PRODUCTS})} - \sum m S^\circ_{(\text{REACTANTS})}$$

SAMP. EX. 19.5 pg 829 CALC.  $\Delta S^\circ_{\text{RXN}}$  FOR  $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$\text{H}_2$   $S^\circ = 130.6 \text{ J/K}\cdot\text{mol}$

$\text{N}_2$   $S^\circ = 192 \text{ J/K}\cdot\text{mol}$

$\text{NH}_3$   $S^\circ = 192.5 \text{ J/K}\cdot\text{mol}$

$$\Delta S^\circ_{\text{RXN}} = 2(192.5) - [3(130.6) + 1(192)]$$

$$= -198.8 \text{ J/K}$$

NOTE:  $S$  DECREASES AS THE RXN GOES FROM 4 mol GAS TO 2 mol GAS

TO GET A FEEL FOR HOW ENTROPY WORKS IT'S HELPFUL TO CONSIDER SOME QUALITATIVE DISCUSSIONS OF  $\Delta S$  FOR VARIOUS SITUATIONS.

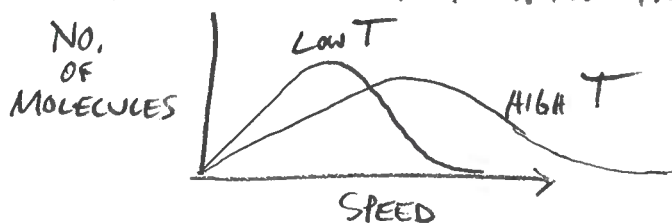
## How $\Delta S$ depends on $\Delta T$

IF TEMP. INCREASES, ENTROPY INCR. (FOR  $+\Delta T$ ,  $\Delta S$  IS  $+$ )

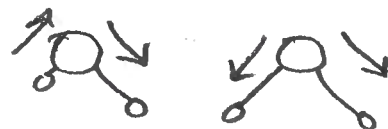
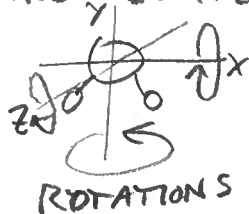
IF TEMP. DECREASES, ENTROPY DECR. (FOR  $-\Delta T$ ,  $\Delta S$  IS  $-$ )

THIS IS FOR TWO REASONS:

1. AS TEMP. INCREASES THE NUMBER OF AVAILABLE SPEEDS A MOLECULES MAY HAVE INCREASES:



2. AT HIGHER TEMP MOLECULES VIBRATE MORE VIGOROUSLY, REPRESENTING AN INCR. IN AVAIL. MICRO STATES:



VIBRATIONS

SEE MODELS 360 FROM THE CHEMED DL SITE ONLINE

## How $\Delta S$ depends on $\Delta V$

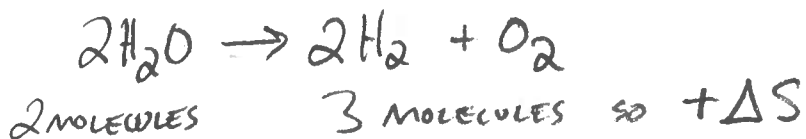
AN INCR. IN VOLUME MEANS MORE AVAILABLE MICROSTATES SO IF  $\Delta V$  IS POSITIVE,  $\Delta S$  WILL BE POSITIVE, AND IF  $\Delta V$  IS  $-$ ,  $\Delta S$  IS ALSO  $-$ .

FOR EXAMPLE, ENTROPY INCR. WHEN A GAS EXPANDS OR IS FORMED IN A CHEMICAL RXN. ENTROPY INCR. WHEN A SOLID DISSOLVES: AS THE PARTICLES DISSOLVE THE AVAIL. VOL. INCREASES.

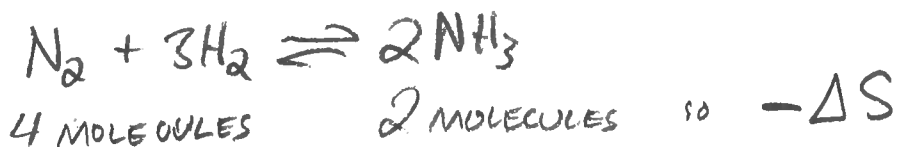
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## How $\Delta S$ DEPENDS ON $\Delta n$

IN CHEMICAL REACTIONS THE TOTAL NUMBER OF MOLECULES MAY CHANGE. ANY INCR. IN THE NO. OF PARTICLES GIVES A + VALUE FOR  $\Delta S$ :



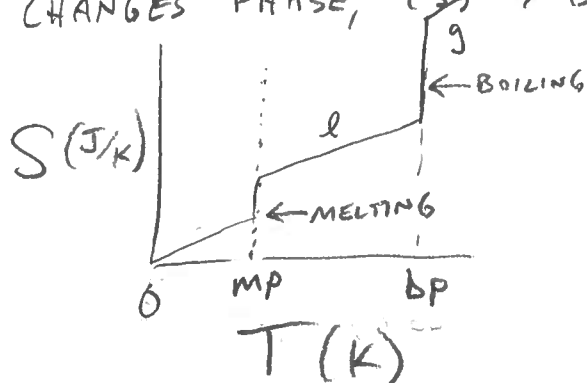
ANY DECR. IN THE NO. OF PARTICLES GIVES A - VALUE FOR  $\Delta S$ :



## How S DEPENDS ON THE DISTRIBUTION OF ENERGY

IF ENERGY IS CONCENTRATED IN A SMALL VOLUME OR WITH A SMALL NO. OF PARTICLES IT IS A LOW-ENTROPY SITUATION. SO IF PARTICLES SPREAD OUT, OR EVEN IF THEIR ENERGY IS TRANSFERRED TO A LARGER POPULATION, IT WILL REPRESENT AN INCREASE IN ENTROPY. FOR EX, IF ONE END OF A METAL BAR IS HEATED THEN AT THAT END ATOMS VIBRATE MORE INTENSELY. AS THE FAST-VIBRATING ATOMS COLLIDE WITH SLOWER NEIGHBORS THE HEAT IS CONDUCTED AWAY UNTIL IT IS UNIFORMLY DISTRIBUTED IN THE BAR.

AS A TEST CASE, CONSIDER HOW S CHANGES AS A SUBSTANCE CHANGES PHASE, (s)  $\rightarrow$  (l)  $\rightarrow$  (g).



S INCR. AS T INCREASES (LINES SLOPE UP). THERE IS A BIG JUMP IN S FROM (s) TO (l) AS FREEDOM OF MOVEMENT INCREASES.

THERE IS A VERY LARGE JUMP US IN S FROM (l) TO (g) B/C VOLUME INCREASES SO MUCH, IN ADDITION TO GREATER MOVEMENT FREEDOM.

# SPONTANEITY IN CHEMICAL AND PHYSICAL CHANGES

THE THERMODYNAMIC FAVORABILITY

THERE ARE TWO THINGS CHEMISTS WANT FROM THIS THEORY OF THERMODYNAMICS:

1. UNDER WHAT CONDITIONS A PROCESS IS SPONTANEOUS
2. HOW MUCH ENERGY IS RELEASED OR ABSORBED BY A PROCESS, TAKING ENTROPY INTO ACCOUNT

TO ANSWER THE FIRST QUESTION ONE MIGHT THINK THAT ANY PROCESS FOR WHICH ENTROPY INCREASES WOULD BE SPONTANEOUS. IN OTHER WORDS IF  $\Delta S$  IS  $+$  A PROCESS IS SPON. FOR EXAMPLE, DESPITE THE ENTHALPY OF SOLUTION FOR  $KNO_3$  BEING POSITIVE, IT DISSOLVES READILY DUE TO THE LARGE INCR. IN ENTROPY AS THE IONS SPREAD THROUGHOUT THE SOLUTION. ON THE OTHER HAND, ENTROPY DECREASES ( $-\Delta S$ ) FOR A LIQUID THAT FREEZES, BUT THIS HAPPENS SPONTANEOUSLY BELOW THE MELTING POINT.

THE ANSWER TO THIS AMBIGUITY IS THAT IT ISN'T JUST  $\Delta S_{sys}$  THAT MATTERS: THE ENTROPY OF THE SURROUNDINGS ALSO CHANGES ( $\Delta S_{surr}$ ). ADD THESE TOGETHER AND YOU HAVE THE ENTROPY CHANGE OF THE UNIVERSE:

$$\Delta S_{UNIV} = \Delta S_{SYS} + \Delta S_{SURR}$$

AS LONG AS THIS SUM IS POSITIVE, A PROCESS IS SPON. THAT'S THE SECOND LAW.

THE QUANTITIES  $\Delta S_{UNIV}$  AND  $\Delta S_{SURR}$

CAN BE HARD TO MEASURE. TO BE USEFUL, ALL THE VARIABLES WE USE NEED TO BE BASED ON THE SYSTEM. SO, WE DEFINE A NEW QUANTITY, THE GIBBS FREE ENERGY

OR  $\Delta G$ :  $\Delta G_{SYS} = -W_{max}$

$W_{max}$  IS THE MAXIMUM WORK A SYSTEM COULD DO AT 100% EFFICIENCY.

( $W_{max}$  IS NEG. B/C FROM THE SYSTEM'S POINT OF VIEW THE ENERGY LEAVES THE SYSTEM).

NOW, WE'LL USE  $\Delta G_{sys}$  TO REDEFINE  $\Delta S_{univ}$ :

$$\Delta S_{univ} = \frac{-\Delta G_{sys}}{T}$$

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

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

(THIS WAS ITS DEFINITION ALREADY)

NOW, LET'S RE-WRITE THE SECOND LAW:

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} \quad (> 0)$$

$$\left( \Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys} \right) \times (-T)$$

MULTIPLY THROUGH BY  $-T$

SUBSTITUTE  $-\frac{\Delta G}{T}$

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

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

THIS IS THE FUNDAMENTAL EQUATION OF CHEMICAL THERMODYNAMICS.

FOR  $+\Delta S_{univ}$  THE VALUE OF  $\Delta G$  IS NEGATIVE AND A PROCESS IS SPONTANEOUS

FOR  $-\Delta S_{univ}$  THE VALUE OF  $\Delta G$  IS POSITIVE AND A PROCESS IS NON-SPON.

$\Delta G < 0 \rightarrow$  SPONTANEOUS A.K.A. THERMODYNAMICALLY

$\Delta G = 0 \rightarrow$  AT EQUILIBRIUM  $\star$  FAVORABLE

$\Delta G > 0 \rightarrow$  SPON. IN REVERSE

(11)

$\Delta G$  (NO CIRCLE) MEANS THE CHANGE IN FREE ENERGY UNDER ARBITRARY CONDITIONS (NOT NECESSARILY  $P=1\text{atm}$ ,  $[X]=1\text{M}$ ,  $T=298\text{K}$  OR STANDARD CONDITIONS.)

$\Delta G^\circ$  (WITH A CIRCLE) MEANS THE CHANGE IN FREE ENERGY UNDER STANDARD CONDITIONS.

JUST AS YOU CAN CALC.  $\Delta H^\circ_{\text{RXN}}$  USING ENTHALPY OF FORMATION VALUES (SEE APPENDIX C) YOU CAN CALC.

$\Delta G^\circ_{\text{RXN}}$  USING FREE ENERGY OF FORMATION VALUES, WHICH IS THE FREE ENERGY RELEASED OR ABSORBED UPON FORMATION OF 1 mol OF A SUBSTANCE FROM ITS ELEMENTS UNDER STANDARD CONDITIONS.

AS WITH  $\Delta H^\circ_f$ ,  $\Delta G^\circ_f = 0$  FOR PURE ELEMENTS.

$$\Delta G^\circ_{\text{RXN}} = \sum n \Delta G^\circ_f(\text{PRODUCTS}) - \sum m \Delta G^\circ_f(\text{REACTANTS})$$

ANOTHER WAY TO CALC.  $\Delta G^\circ_{\text{RXN}}$  IS TO USE KNOWN VALUES FOR  $\Delta H^\circ_{\text{RXN}}$  AND  $\Delta S^\circ_{\text{RXN}}$  (IF YOU HAVE THEM) AND USE  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  AT 298K. YOU CAN USE  $\Delta H^\circ$  AND  $\Delta S^\circ$  VALUES, ALONG WITH A DIFFERENT TEMPERATURE TO CALC. AN APPROX. VALUE FOR  $\Delta G^\circ$  IN ORDER TO JUDGE SPONTANEITY AS TEMP. RISES OR FALLS.

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# THE EFFECT OF TEMPERATURE ON SPONTANEITY

↳ AKA. THERMODYNAMIC FAVORABILITY

WHEN WE LEARNED ABOUT CHEMICAL EQUILIBRIUM WE STUDIED LE CHÂTELLIER'S PRINCIPLE; WITH RESPECT TO WHETHER A RXN WAS ENDO- OR EXOTHERMIC WE SAID REACTANTS OR PRODUCTS WERE FAVORED AS TEMP. ROSE OR FELL. WITH FREE ENERGY ( $G$ ) WE NOW HAVE A WAY TO QUANTIFY THESE CHANGES.

## EXOTHERMIC

$K_{eq}$  DECR AS  $T$  RISES  
OR

AS  $T$  RISES THE RXN BECOMES SPONTANEOUS IN REVERSE ( $+\Delta G$ )

$K_{eq}$  INCR. AS  $T$  FALLS  
OR

AS  $T$  FALLS THE RXN BECOMES SPONTANEOUS FORWARD ( $-\Delta G$ )

## ENDOTHERMIC

$K_{eq}$  INCR AS  $T$  RISES  
OR

AS  $T$  RISES THE RXN BECOMES SPONTANEOUS FORWARD ( $-\Delta G$ )

$K_{eq}$  DECR AS  $T$  FALLS  
OR

AS  $T$  FALLS THE RXN BECOMES SPONTANEOUS IN REVERSE ( $+\Delta G$ )

YOU CAN USE  $\Delta G = \Delta H - T\Delta S$  TO FIND THE TEMP. AT WHICH A RXN IS SPON. NEITHER FORWARD NOR IN REVERSE. FOR  $+\Delta H$ , ANY TEMP ABOVE IS SPON. AND (WHEN  $\Delta G = 0$ ) ANY TEMP BELOW IS SPON. IN REVERSE. FOR  $-\Delta H$ , ANY TEMP ABOVE IS SPON. IN REVERSE AND ANY TEMP BELOW IS SPONTANEOUS. SOME REACTIONS ARE SPON. AT ALL TEMP.S AND SOME AT NO TEMP.

TO DO THIS, LET  $\Delta G = 0$  AND SOLVE FOR T:

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

$$0 = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

AS AN ILLUSTRATION RELEVANT TO THE TABLE BELOW, CONSIDER A DEMONSTRATION OF THIS "REACTION":



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

IF $\Delta H$	AND $\Delta S$	THEN $\Delta G$	WHICH MEANS
-	+	ALWAYS -	A RXN IS SPONTANEOUS AT <u>ALL</u> TEMPERATURES
+	-	ALWAYS +	A RXN IS SPON. AT <u>NO</u> TEMPERATURES (SPON. IN REV.)
-	-	+ <u>OR</u> - DEPENDING ON TEMP.	SPON. AT <u>LOW</u> T (AS WE EXPECT FOR EXOTHERMIC RXNS) <hr/> NON-SPON. AT <u>HIGH</u> T
+	+	+ <u>OR</u> - DEPENDING ON TEMP.	SPON. AT <u>HIGH</u> T (AS WE EXPECT FOR ENDOTHERMIC RXNS) <hr/> NON-SPON. AT <u>LOW</u> T

WHEN  $\Delta H$  AND  $\Delta S$  HAVE THE SAME SIGN:

BOTH + PROCESS IS SPONTANEOUS AT HIGH TEMP SO  $|T\Delta S| > |\Delta H|$

BOTH - PROCESS IS SPONTANEOUS AT LOW TEMP SO  $|T\Delta S| < |\Delta H|$

RE: RUBBER BAND

STRETCHED  $\rightleftharpoons$  CONTRACTED $+\Delta H$  OR  $-\Delta H$ ?  
(TEST TEMP) $+\Delta G$  OR  $-\Delta G$ 

(IS CONTRACTING SPONTANEOUS?)

BASED ON THESE ANSWERS DECIDE  
WHETHER IT'S  $+\Delta S$  OR  $-\Delta S$   
WHEN A RUBBER BAND CONTRACTS?ARE RUBBER BAND MOLECULES MORE ORDERED (OR ORDERLY, THAT IS,  
HAVE LOWER ENTROPY) WHEN STRETCHED OR CONTRACTED? EXPLAIN.

ARE BONDS FORMING OR BREAKING WHEN THE BAND CONTRACTS? EXPLAIN.

IS CONTRACTING MORE SPONTANEOUS AT LOW OR HIGH TEMPERATURE? EXPLAIN.

## FREE ENERGY AND EQUILIBRIUM

SYMBOLS WITH A LITTLE CIRCLE MEAN THEY REPRESENT A VALUE  
UNDER STANDARD CONDITIONS (1 atm, 1 mol/L, 298K). $\Delta G^\circ$   $\Delta H^\circ$   $\Delta S^\circ$ SYMBOLS WITHOUT A CIRCLE ARE FOR VALUES UNDER OTHER  
CONDITIONS. $\Delta G$   $\Delta H$   $\Delta S$ TECHNICALLY,  $\Delta G^\circ$  IS FOR 298K ONLY. HOWEVER, IT IS  
OFTEN USEFUL TO USE  $\Delta H^\circ$  AND  $\Delta S^\circ$ , ALONG WITH SOME  
OTHER TEMPERATURE, TO ESTIMATE  $\Delta G^\circ$  AS IT RESPONDS TO  
A CHANGE IN T.

FOR EXAMPLE, ICE MELTS AT 298K (25°C) SO  $\Delta G^\circ$  IS NEG. FOR THIS PROCESS

$$\Delta H_{\text{fus}}^\circ = +6.02 \text{ kJ/mol} \quad \Delta S_{\text{fus}}^\circ = +22.0 \text{ J/K}$$

$$\text{SO } \Delta G^\circ = +6.02 \frac{\text{kJ}}{\text{mol}} - 298\text{K} \left( \frac{0.0220 \text{ kJ}}{1\text{K}} \right)$$

$$\boxed{\Delta G^\circ = -0.54 \text{ kJ/mol}}$$
 (REGARDLESS OF THE SIZE OR MAGNITUDE,  $\Delta G^\circ$  IS NEGATIVE SO IT IS SPONTANEOUS FOR ICE TO MELT AT 25°C)

WE CAN ESTIMATE  $\Delta G^\circ$  AT 268K (OR -5°C):

$$\Delta G^\circ = 6.02 - 268(0.022)$$

$$\Delta G^\circ = +0.12 \text{ kJ/mol}$$
 (IT'S POSITIVE SO ICE DOES NOT SPONTANEOUSLY MELT AT 268K OR -5°C)

AND AT 273K ICE AND WATER ARE IN EQUILIBRIUM SO IT IS SPONTANEOUS NEITHER TO MELT NOR TO FREEZE:

$$\Delta G^\circ = 6.02 - 273(0.022) = \emptyset \text{ (OR CLOSE ENOUGH!)}$$

A FEW PAGES BACK, WHEN  $\Delta G$  WAS DEFINED, IT SAYS THAT AT EQUILIBRIUM,  $\boxed{\Delta G = \emptyset \text{ kJ/mol}}$ .

FOR THIS REASON, YOU CAN EST. A SUBSTANCE'S MELTING POINT BY SETTING  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \emptyset$  AND SOLVING FOR T.

SINCE  $\Delta G$  DOES NOT JUST DEPEND ON T WE NEED A WAY TO ACCOUNT FOR DIFFERENT PRESSURES OR CONCENTRATIONS!

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

$$R = 8.314 \frac{\text{J}}{\text{K mol}}$$

$$T \text{ (IN K)}$$

Q = THE REACTION QUOTIENT

(K<sub>eq</sub> EXPRESSION FILLED IN WITH

INITIAL NOT EQUIL CONCENTRATIONS) (16)

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

$Q = 1$  UNDER STANDARD CONDITIONS (ALL CONC = 1M AND ALL GAS PARTIAL PRESSURES = 1 atm)

SO UNDER STANDARD CONDITIONS,  $\Delta G = \Delta G^\circ$

B/c  $\ln 1 = 0$ . (THIS IS PRETTY LOGICAL).

$\Delta G = 0$  AT EQUILIBRIUM AND WE CAN USE THIS IDEA TO RELATE THE VALUE OF  $K_{eq}$  TO  $\Delta G^\circ$ :

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{NOTE CHANGE}$$

$$0 = \Delta G^\circ + RT \ln K_{eq}$$

$$\text{SO } \boxed{\Delta G^\circ = -RT \ln K}$$

WE CAN RELATE CHANGES TO  $Q$  TO CHANGES IN  $\Delta G$  (AND IN TURN TO SHIFTS OF CONCENTRATIONS AS A SYSTEM MOVES TOWARD EQUILIBRIUM).

REMEMBER, A LOGARITHM OF A FRACTION GIVES A NEGATIVE RESULT

$$\log \frac{1}{10} = \log 10^{-1} = -1$$

A LOGARITHM OF A NUMBER GREATER THAN ONE GIVES A POSITIVE RESULT

$$\log 100 = \log 10^2 = +2$$

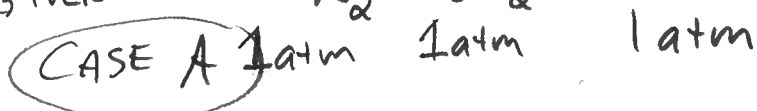
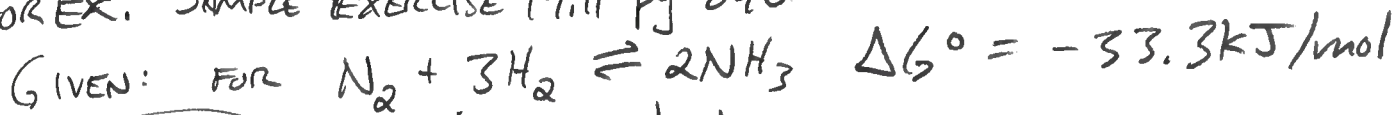
THINKING ABOUT  $\rightarrow \Delta G = \Delta G^\circ + RT \ln Q$  ( $Q = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$ )

UNDER STANDARD CONDITIONS,  $Q = 1$  AND  $\Delta G = \Delta G^\circ$

WHEN  $Q < 1$  THE RXN IS HEAVIER ON REACTANT CONC. SO THE RXN SHIFTS RIGHT. SINCE  $\ln Q$  IS NEG, THE VALUE OF  $\Delta G$  GOES DOWN, MEANING THE FORWARD REACTION IS MORE SPONTANEOUS.

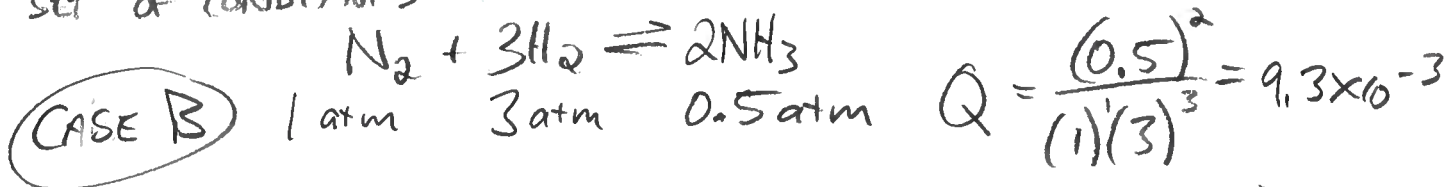
WHEN  $Q > 1$  THE REACTION IS HEAVIER ON PRODUCT CONC SO THE RXN SHIFTS LEFT. SINCE  $\ln Q$  IS POSITIVE, THE VALUE OF  $\Delta G$  GOES UP, MEANING THE FORWARD REACTION IS LESS SPONTANEOUS.

FOREX. SAMPLE EXERCISE 19.11 pg 840



$$\Delta G = \Delta G^\circ + RT \ln Q = -33.3 \text{ kJ/mol} + RT \ln(1) = -33.3 \text{ kJ/mol}$$

COMPARE THIS TO  $\Delta G$  AS CALC. FOR THE FOLLOWING SET OF CONDITIONS:



$$\Delta G = -33.3 \frac{\text{kJ}}{\text{mol}} + (8.314 \times 10^{-3} \frac{\text{kJ}}{\text{mol}})(298 \text{ K}) \ln(9.3 \times 10^{-3})$$

$$\Delta G = -44.9 \text{ kJ/mol}$$

NOTE UNITS!

SINCE  $\Delta G$  FOR CASE B IS MORE NEGATIVE, THE RXN IS MORE SPONTANEOUS FORWARD. THIS IS CONSISTENT

WITH LE CHÂTELIER'S PRINCIPLE SINCE IN CASE B WE HAVE INCR. A REACTANT CONC. RELATIVE TO CASE A AND WE HAVE DECR. A PRODUCT CONC. REL. TO CASE A.

$$\begin{array}{c} -33.3 \\ \downarrow \\ -44.9 \end{array}$$

SO WE CAN USE THIS EQN ( $\Delta G = \Delta G^\circ + RT \ln Q$ ) TO HELP US SEE HOW CHANGING CONDITIONS AFFECTS A CHEMICAL RXN.

THE SAME EQUATION CAN BE EMPLOYED TO SEE HOW THE VALUE OF  $K_{eq}$  DEPENDS ON TEMPERATURE. WE EXPLORED THIS QUALITATIVELY WITH LE CHÂTELIER'S PRINCIPLE IN CH. 15 FOR EXO- AND ENDOOTHERMIC RXNS.

# THE RELATIONSHIP BTWN $\Delta G^\circ$ AND $K_{eq}$

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

AT EQUILIBRIUM,  $\Delta G = 0$  AND  $Q = K_{eq}$ :

$$0 = \Delta G^\circ + RT \ln K$$

$$\text{SO } \boxed{\Delta G^\circ = -RT \ln K} \quad \text{AND } K = e^{-\left(\frac{\Delta G^\circ}{RT}\right)}$$

LET'S SEE WHAT WE CAN DO WITH THIS.

SAY WE WOULD LIKE TO ESTIMATE THE VALUE OF  $K_{eq}$  AT TWO TEMPERATURES. HERE IS HOW WE WOULD PROCEED:



WE HAVE AT 298K:  $\Delta H^\circ = -92.38 \text{ kJ/mol}$

$$\Delta S^\circ = -198.3 \text{ J/Kmol}$$

$$\Delta G^\circ = \left(-92.38 \frac{\text{kJ}}{\text{mol}}\right) - (298\text{K})\left(-0.1983 \frac{\text{kJ}}{\text{Kmol}}\right)$$

$$\Delta G_{298}^\circ = -33.29 \text{ kJ/mol}$$

SO FOR STANDARD CONDITIONS,  $K_{eq} = e^{-\left(\frac{-33.29 \text{ kJ}}{8.314 \times 10^{-3} \text{ kJ/Kmol} \cdot 298\text{K}}\right)}$

$$K_{eq} = 6.8 \times 10^5$$

IN ORDER TO EST.  $K_{eq}$  AT THE INDUSTRIALLY-EMPLOYED TEMP. OF 873K (600°C) WE FIRST NEED TO EST.  $\Delta G^\circ$  FOR THE HIGHER TEMP.:

$$\Delta G_{873}^\circ = \left(-92.38 \frac{\text{kJ}}{\text{mol}}\right) - (873\text{K})\left(-0.1983 \frac{\text{kJ}}{\text{Kmol}}\right) = +80.74 \text{ kJ/mol}$$

NOTE: WE ASSUME  $\Delta H^\circ$  AND  $\Delta S^\circ$  ARE UNCHANGED. THIS IS ONLY OKAY B/C WE JUST WANT TO ESTIMATE  $\Delta G_{873}^\circ$ .

$$\Delta G_{298}^{\circ} = -33.29 \text{ kJ/mol} \quad K_{eq} = 6.8 \times 10^5$$

$$\Delta G_{873}^{\circ} = +80.74 \text{ kJ/mol} \quad K_{eq} = e^{-\left(\frac{80,740 \text{ J/mol}}{8.314 \text{ J/mol} \cdot 873 \text{ K}}\right)}$$

$$K_{eq} = 1.5 \times 10^{-5}$$

So, at the temp. used for the large-scale production of  $\text{NH}_3$ , the rxn is spontaneous in reverse and so has an equil. constant which favors reactants. Why would this be?

The reason is that, although thermodynamics is important, it isn't the whole story. At 298K this reaction is too slow: none of the molecules have enough kinetic energy to react. None are above the activation energy. To make it fast enough to collect products it has to be a lot hotter! To make up for the positive value of  $\Delta G$  at the higher temp. measures are taken to remove  $\text{NH}_3$  from the reaction while boosting the conc. of  $\text{H}_2$  and  $\text{N}_2$ . In other words, make the value of  $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$  as small as possible. In this way

$\Delta G$  (not  $\Delta G^{\circ}$ ) can be lowered:  $\Delta G = \Delta G^{\circ} + RT \ln Q$   
 B/c  $\ln Q$  is a negative number.

