CHEMICAL THERMODYNAMICS; ΔH, ΔS AND ΔG

A BASIC GOAL OF CHEMISTRY IS TO PREDICT WHETHER OR NOT A REACTION WILL OCCUR WHEN REACTANTS ARE MIXED THAT IS, IS THE REACTION SPONTANEOUS?

CHEMISTS USE THE TECHNIQUES OF THERMODYNAMICS TO ANSWER THIS QUESTION. WE EMPLOY THE QUANTITIES ΔH, ENTHALPY, ΔS, ENTROPY AND ΔG, FREE ENERGY

ΔH, THE ENTHALPY CHANGE

FOR A REACTION CARRIED OUT AT CONSTANT PRESSURE AND TEMPERATURE, THE HEAT OR ENERGY FLOW IS EQUAL TO THE DIFFERENCE IN ENTHALPY BETWEEN PRODUCTS AND REACTANTS

$$\Delta H = H_{PRODUCTS} - H_{REACTANTS} = \text{HEAT FLOW (CONST } T, P)$$

WE DISTINGUISH BETWEEN ENDOTHERMIC REACTIONS: ΔH IS POSITIVE, HEAT FLOWS FROM THE SURROUNDINGS INTO THE SYSTEM, AND ENTHALPY OF PRODUCTS > ENTHALPY OF REACTANTS

AND

EXOTHERMIC REACTIONS ΔH IS NEGATIVE, HEAT FLOWS FROM THE REACTION INTO THE SURROUNDINGS AND $H_{REACTANTS} > H_{PRODUCTS}$

THE ENTHALPY CHANGE FOR A REACTION CAN BE CALCULATED FROM MOLAR HEATS OF FORMATION, ΔH_F

THE MOLAR HEAT OF FORMATION OF A COMPOUND IS THE ENTHALPY CHANGE WHEN 1 MOLE OF THE COMPOUND IS FORMED FROM THE ELEMENTS.

ΔH_F AND ALL THE OTHER USEFUL THERMODYNAMIC QUANTITIES ARE TABULATED IN YOUR BOOK, APPENDIX C

THE ENTROPY OF A SUBSTANCE IS A MEASURE OF HOW "ORDERED" THE SUBSTANCE IS. LOW ENTROPY IS ASSOCIATED WITH HIGHLY ORDERED SUBSTANCES AND HIGH ENTROPY WITH HIGHLY DISORDERED SUBSTANCES

CRYSTALS → HIGH ORDER → LOW ENTROPY

GASES → LOW ORDER → HIGH ENTROPY

THE ENTROPY CHANGE ASSOCIATED WITH A REACTION IS:

$$\Delta S = S_{PRODUCTS} - S_{REACTANTS}$$

FOR INSTANCE, THE PHASE CHANGE

$$H_2O_{(s)} \rightarrow H_2O_{(\ell)} \qquad \Delta S \text{ IS POSITIVE}$$

CLEARLY, ABOVE $0 °C$, THIS PROCESS IS SPONTANEOUS SO, ΔS COMPENSATES FOR THE ENDOTHERMIC ΔH

STANDARD MOLAR ENTROPIES

ABSOLUTE VALUES FOR THE ENTROPY OF A SUBSTANCE CAN BE OBTAINED. WE DEFINE THE ENTROPY OF A PURE SUBSTANCE, AT ABSOLUTE ZERO $(T = 0°K)$ TO BE 0

STANDARD MOLAR ENTROPIES $S°$ ARE MEASURED IN JOULES/$°K$ (MOLE) AND ARE EQUAL TO THE ENTROPY OF ONE MOLE OF A SUBSTANCE IN ITS STANDARD STATE.
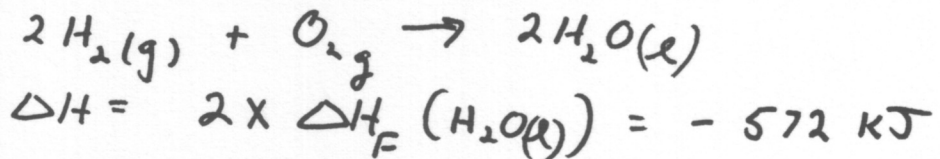
FOR A SUBSTANCE → PURE SUBSTANCE, 1 ATM, $25 °C$
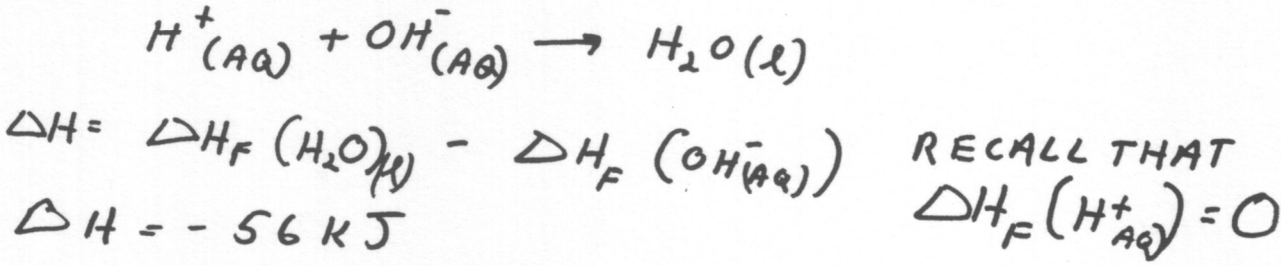
FOR A DISSOLVED SPECIES → 1 M SOLUTION $25 °C$

SOLIDS HAVE LOWER ENTROPY THAN LIQUIDS, WHICH IN TURN, HAVE LOWER ENTROPY THAN GASES

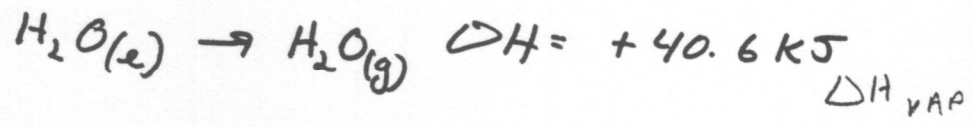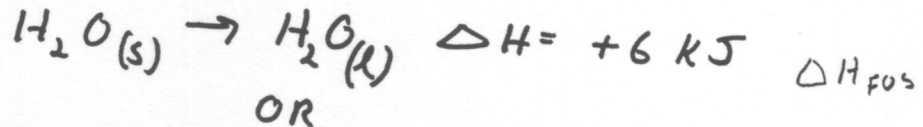|		
$S_i (s)$	18.7 J/k	
$H_2O_{(\ell)}$	69.9 J/k	$S°$ VALUES
$SO_2(g)$	249 J/k	

IT IS TEMPTING TO SAY "EXOTHERMIC REACTIONS ARE
SPONTANEOUS AND ENDOTHERMIC REACTIONS ARE NOT"
(P TO ABOUT 100 YEARS AGO THIS WAS THE PREVAILING IDEA
FOR EXAMPLE :

$$2 H_2(g) + O_{2_g} \rightarrow 2 H_2O(\ell)$$

$$\Delta H = 2 \times \Delta H_F (H_2O(\ell)) = -572 \, kJ$$

OR THE NEUTRALIZATION REACTION :

$$H^+_{(AQ)} + OH^-_{(AQ)} \rightarrow H_2O(\ell)$$

$$\Delta H = \Delta H_F (H_2O)_{(\ell)} - \Delta H_F (OH^-_{(AQ)})$$ RECALL THAT

$$\Delta H = -56 \, kJ$$ $$\Delta H_F (H^+_{AQ}) = 0$$

HOWEVER, THIS SIMPLE RULE FAILS RATHER OFTEN
FOR EXAMPLE, WITH PHASE CHANGES :

$$H_2O(s) \rightarrow H_2O_{(\ell)} \quad \Delta H = +6 \, kJ \quad \Delta H_{FUS}$$

OR

$$H_2O_{(\ell)} \rightarrow H_2O_{(g)} \quad \Delta H = +40.6 \, kJ \quad \Delta H_{VAP}$$

ALSO, THIS REACTION :

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad \Delta H = +178 \, kJ$$

IS NON SPONTANEOUS AT ROOM TEMPERATURE, BUT
SPONTANEOUS AT $1100°K$ EVEN THOUGH ΔH IS STILL
$+178 kJ$.
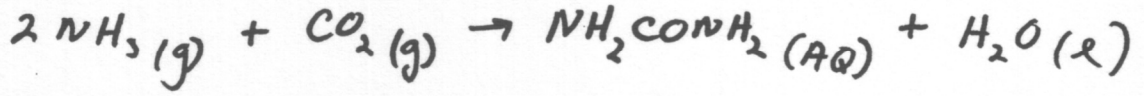
TO DECIDE WHETHER A GIVEN REACTION WILL BE
SPONTANEOUS AT A GIVEN TEMPERATURE AND PRESSURE,
WE MUST CONSIDER ANOTHER FACTOR, THE ENTROPY
CHANGE, ΔS

IN A REACTION, THE SIGN OF ΔS CAN OFTEN BE PREDICTED USING THE FOLLOWING GUIDE:

ENTROPY INCREASES WHEN:
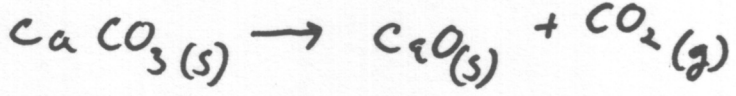
1) A MOLECULE IS BROKEN INTO TWO OR MORE MOLECULES

2) A REACTION PRODUCES AN INCREASE IN MOLES OF GAS

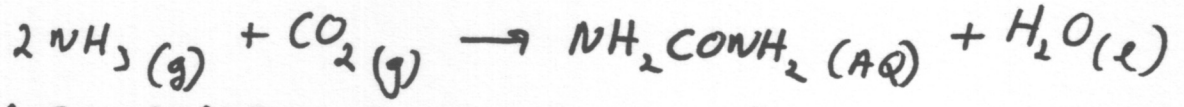3) A SOLID $\rightarrow$ LIQUID OR LIQUID $\rightarrow$ GAS

FOR EXAMPLE

$$2 NH_3 (g) + CO_2 (g) \rightarrow NH_2 CONH_2 (AQ) + H_2O (\ell)$$

AND

$$\Delta S \text{ IS}$$

$$Ca CO_3 (s) \rightarrow CeO_{(s)} + CO_2 (g)$$

QUANTITATIVELY

$$\Delta S \text{ IS}$$

$$\Delta S° = S°_{PRODUCTS} - S°_{REACTANTS}$$

USING THE TABLE IN   CALCULATE THE ENTROPY CHANGE FOR THIS REACTION:

$$2 NH_3 (g) + CO_2 (g) \rightarrow NH_2 CONH_2 (AQ) + H_2O (\ell)$$

STANDARD ENTROPIES $S°$

$$NH_3 (g) \qquad 193 \text{ J/k}$$
$$CO_2 (g) \qquad 214 \text{ J/k}$$
$$NH_2 CONH_2 (AQ) \qquad 174 \text{ J/k}$$
$$H_2O (\ell) \qquad 70 \text{ J/k}$$

$$2 \times (193) + 214 - (174 + 70) =$$

$$\Delta S° = \Sigma n S°_{PROD} - \Sigma n S°_{REACT}$$

$$\Delta S° = (174 + 70) - (2 \times 193 + 214)$$

$$\Delta S° = 244 - 600$$

$$\Delta S° = -356 \text{ J/k}$$

ENTROPY CHANGE FOR A PHASE TRANSITION

BECAUSE PHASE TRANSITIONS ARE EQUILIBRIUM

PROCESSES, THE INCREASE IN ENTROPY RESULTS ONLY

FROM ABSORPTION OF HEAT.

FOR THE MELTING OF ICE, THAT HEAT IS HEAT OF

FUSION, ΔH_f

$$\Delta S = \frac{\Delta H_f}{T} = \frac{6.3 \times 10^3 \, J}{273} = 22 \, J/K$$

USING THE TABLES, YOU CAN

NOW CALCULATE ΔS FOR ANY PHASE TRANSITION

AND, THE ABOVE RELATIONSHIP CAN BE USED TO

RELATE ΔS, ΔH, AND T

TO DO SO, WE INTRODUCE A NEW TERM G, THE

GIBBS <u>FREE ENERGY</u>. G IS DEFINED AS G = H - TS

AND, MORE USEFULLY, $\Delta G = \Delta H - T \Delta S$

THE CHANGE IN FREE ENERGY, ΔG IS THE FINAL

MEASURE OF SPONTANEITY IN A REACTION. IF ΔG

IS <u>NEGATIVE</u>, THE REACTION IS <u>SPONTANEOUS</u>. IF ΔG

IS <u>POSITIVE</u>, THE REACTION IS <u>NON SPONTANEOUS</u>.

THE STANDARD FREE $\Delta G° = \Delta H° - T \Delta S°$ FOR

SUBSTANCES IN THE STANDARD STATE.

AND, FOR A REACTION, $\Delta G = G_{PRODUCTS} - G_{REACTANTS}$

IN OTHER WORDS, ΔG IS A MEASURE OF THE DRIVING

FORCE OF A REACTION. REACTIONS, AT CONSTANT T AND P,

GO IN SUCH A DIRECTION AS TO <u>DECREASE</u> THE FREE

ENERGY OF THE SYSTEM. SO, THE DIRECTION OF A REACTION

IS DETERMINED BY THE RELATIVE FREE ENERGIES OF

PRODUCTS AND REACTANTS.

YOU CAN USE STANDARD FREE ENERGIES ΔG_F^0 WHICH
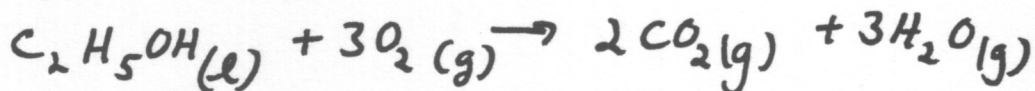HAVE BEEN TABULATED   APPENDIX C

$$\Delta G^0 = \sum m \, \Delta G_F^0 \text{ PROD} - \sum m \, \Delta G_F^0 \text{ REACT}$$

FOR EXAMPLE:

CALCULATE ΔG^0 FOR THE COMBUSTION OF 1 MOLE OF
ETHANOL (C_2H_5OH) AT $25^\circ C$ AND 1ATM

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

$$\Delta G^0 = \sum m \, \Delta G_{F\,PROD}^0 - \sum m \, \Delta G_{F\,REACT}^0$$

ΔG_F^0 FROM TABLE 18.2 IN KJ/MOLE

C_2H_5OH -174.8
  O_2 0 $\longrightarrow$ ΔG^0 FOR ELEMENTS $= 0$
  CO_2 -394.4
  H_2O -228.6

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_2\,g + 3H_2O_{(g)}$$
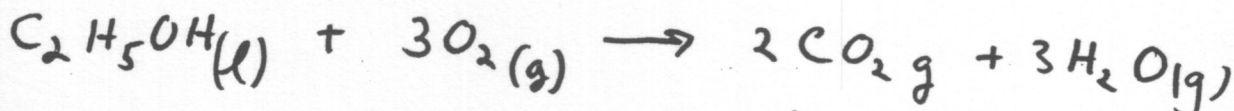
ΔG_F^0 -174.8   0 $2(-394.4)$ $3(-228.6)KJ$

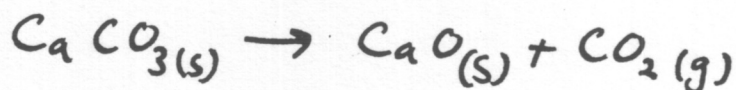$$\Delta G^0 = \sum m \, \Delta G_F^0 \text{ PROD} - \sum m \, \Delta G_F^0 \text{ REACT}$$

$$\Delta G^0 = 2(-394.4) + 3(-228.6) - (-174.8)$$

$$= -788.8 + -685.8 + 174.8$$

$$\Delta G^0 = -1299 \text{ KJ}$$

THE LARGE NEGATIVE ΔG^0 INDICATES A VERY SPONTANEOUS RXN

CALCULATE ΔG^0 FOR THE FOLLOWING REACTION

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

           ΔG_F^0

$CaCO_3$ -1128.8 $\Delta G^0 = -603.5 - 394.4 - (-1128.8)$

CaO -603.5

CO_2 -394.4 $\Delta G^0 = +130.9 \text{ KJ}$

WHAT IS THE STANDARD FREE ENERGY CHANGE, $\Delta G°$, FOR THE FOLLOWING REACTION

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

CALCULATE $\Delta H°$ AND $\Delta S°$

$\underline{\Delta H°}$
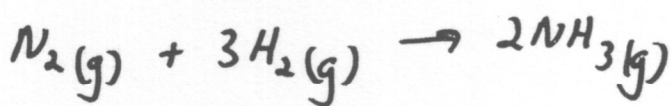
	$N_2(g)$	$+ 3H_2(g) \rightarrow$	$2NH_3(g)$
$\Delta H_F°$	0	0	$2(-45.9 \text{ KJ})$
$S°$	191.5	$+(3)(130.6)$	$2(193) \text{ J/K}$

$\Delta H° = \Sigma \Delta H_{f PROD} - \Sigma \Delta H_{f REACT}$

$\quad = -91.8 KJ - 0$

$\Delta H° = -91.8 KJ$

$\underline{\Delta S°}$

$\Delta S° = \Sigma m \Delta S°_{PROD} - \Sigma m \Delta S°_{REACT}$

$\Delta S° = 2(193) - (191.5 + 3(130.6))$

$\quad = 386 - 583.3$

$\Delta S° = -197.3 \text{ J/K}$

$\underline{\Delta G°}$

SUBSTITUTE INTO $\Delta G°$ EQUATION $\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = -91.8 KJ - (298)(0.197 KJ/K)$

$\quad = -91.8 - -58.7$

$\Delta G° = -33.1 KJ$

MEANING A SPONTANEOUS REACTION

LOOKING AGAIN AT THE RELATIONSHIP BETWEEN ENTHALPY, ENTROPY AND FREE ENERGY
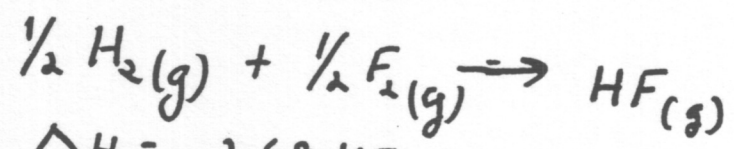
$$\Delta G = \Delta H - T \Delta S$$

SO ΔG DEPENDS ON TWO QUANTITES, THE ENTHALPY CHANGE DUE TO THE MAKING AND BREAKING OF BONDS, AND THE PRODUCT OF THE CHANGE IN RANDOMNESS (ΔS) AND T

THERE ARE TWO FACTORS WHICH TEND TO MAKE ΔG NEGATIVE AND THEREFORE LEAD TO A SPONTANEOUS REACTION

    1) A NEGATIVE VALUE FOR ΔH (EXOTHERMIC)

    2) A POSITIVE VALUE OF ΔS (PROD LESS ORDERED THAN REACT)

EXAMPLES WHERE ENTROPY IS THE DRIVING FORCE

    1) FORMATION OF A SOLUTION $\Delta H \approx 0$ ΔS POSITIVE

    2) MELTING AND VAPORIZING $\Delta H +$, $\Delta S +$
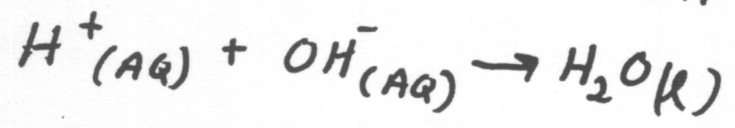
  , SOME REACTIONS ΔH DOMINATES AND ΔS IS NEAR ZERO

$$\tfrac{1}{2} H_2{}_{(g)} + \tfrac{1}{2} F_2{}_{(g)} \longrightarrow HF_{(g)}$$

$$\Delta H = -268 \ KJ$$

$$\Delta S = 0.01 \ KJ/°K$$

MORE COMMONLY, BOTH $\Delta H, \Delta S$ MAKE CONTRIBUTIONS TO ΔG

SOME EXAMPLES:

  CALCULATE $\Delta S°$ AND $\Delta G°$ FOR THIS REACTION: $\Delta H = -55.9 \ KJ$

$$H^+{}_{(AQ)} + OH^-{}_{(AQ)} \longrightarrow H_2O{}_{(\ell)}$$

$$\Delta S° = S°(H_2O_{(\ell)}) - \left(S°H^+{}_{(AQ)} + S°OH^-{}_{AQ} \right)$$

$$\Delta S° = 69.9 \ J/k - (0 + -10.5 \ J/k)$$

$$\Delta S° = 80.4 \ J.k$$

$$\Delta G° = \Delta H - T\Delta S = -55.9 \ KJ - (298)(0.084 \ KT) = -79.9 \ KJ$$

EFFECT OF T UPON REACTION SPONTANEITY

INCREASING T MAY OR MAY NOT CHANGE THE DIRECTION IN WHICH THE REACTION PROCEEDS SPONTANEOUSLY. IT DEPENDS ON THE RELATIVE SIGNS OF ΔH AND ΔS

IF ΔH AND ΔS HAVE THE OPPOSITE SIGN, IT IS IMPOSSIBLE TO REVERSE THE DIRECTION OF SPONTANEITY BY A CHANGE IN T, BECAUSE THE TWO TERMS, ΔH AND $-T\Delta S$ REINFORCE EACH OTHER

IF ΔH AND ΔS HAVE THE SAME SIGNS, THE DIRECTION OF SPONTANEITY REVERSES AND ΔG CHANGES SIGN AS TEMPERATURE INCREASES

HENCE, FOR ICE MELTING AND WATER VAPORIZING

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \rightarrow H_2O_{(g)}$$
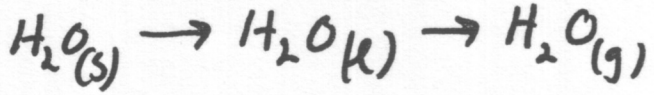
$$\Delta S = +22 \, J/K \qquad \Delta S = +118 \, J/K$$
$$\Delta H = +6.5 \, kJ \qquad \Delta H = +40.6 \, kJ$$

SO, FOR ICE, AT LOW TEMPERATURE ΔH DOMINATES BUT AT HIGHER TEMPERATURE $-T\Delta S$ DOMINATES, ΔG CHANGES FROM + TO - AND ENTROPY DRIVES THE PHASE CHANGE.

SUMMARIZING

$\Delta H°$	$\Delta S°$	$\Delta G°$	COMMENTS
-	+	-	SPONTANEOUS AT ALL T
+	-	+	NON SPONTANEOUS AT ALL T
-	-	+ OR -	SPONTANEOUS AT LOW T NON SPONTANEOUS AT HIGH T
+	+	+ OR -	NON SPONTANEOUS AT LOW T SPONTANEOUS AT HIGH T

AS ANOTHER EXAMPLE OF A REACTION FOR WHICH ΔH
AND ΔS HAVE THE SAME SIGN:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$
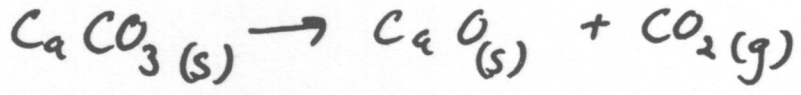
$$\Delta H = 178 \, KJ$$
$$\Delta S = 160.4 \, J/k$$

SO $\Delta G^\circ = 178 \, KJ - T(160.4 \, J/k)$

NOW WE WILL ASSUME THAT ΔH AND ΔS DO NOT
CHANGE WITH TEMPERATURE (ONLY APPROXIMATELY TRUE)
WHEN A REACTION IS COMPLETE, $\Delta G = 0$

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

SOLVE FOR T

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

$$T = \frac{178 \, KJ}{160.4 \, J/k} = 1121^\circ K$$

THIS IS THE TEMPERATURE WHERE $CaCO_3$ BEGINS
TO DECOMPOSE

FINALLY, RELATING ΔG TO THE EQUILIBRIUM CONSTANT K

ΔG IS RELATED TO K AS FOLLOWS

$$\Delta G^\circ = -RT \ln K$$

OR, AT 25°C $\quad \Delta G^\circ = -5.71 \log K$ (AT 25°C

IF ΔG IS NEGATIVE, LOG K IS POSITIVE $\rightarrow$ SPONTANEOUS
IF ΔG IS POSITIVE, LOG K IS NEGATIVE $\rightarrow$ NONSPONTANEOUS
IF ΔG IS 0 LOG K = 0 K = 1 $\rightarrow$ AT EQUILIBRIUM

MORE QUANTITATIVELY, RELATIONSHIP BETWEEN ΔG° AND K

AT 25°C

ΔG° (KJ)	-120	-80	-40	0	40	80	120
K		1×10^{21}	1×10^{14}	1×10^{7}	1	1×10^{-7}	1×10^{-14}	1×10^{-21}

AS AN EXAMPLE OF THIS TYPE OF CALCULATION:

CALCULATE ΔG° AT 25°C

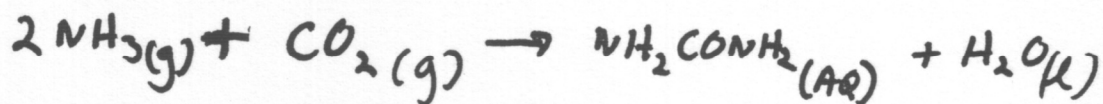$$H^+_{(AQ)} + OH^-_{(AQ)} \rightarrow H_2O \quad K_w = 1\times10^{-14}$$

$$\Delta G^\circ = -5.71 \times LOG K$$
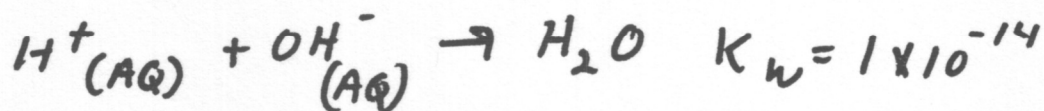
$$LOG x = 14$$

$$\Delta G^\circ = -5.71 \times 14.00 = -79.9 KJ \text{ (AS PREVIOUSLY CALCULATED FROM } \Delta G^\circ = \Delta H - T\Delta S)$$

NOW CALCULATE K FROM ΔG°

FOR THE REACTION:

$$2NH_{3(g)} + CO_{2(g)} \rightarrow NH_2CONH_{2(AQ)} + H_2O_{(l)}$$
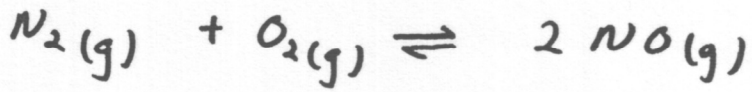
$$\Delta G^\circ = -13.6 KJ$$

$$\Delta G^\circ = -5.71 \log K$$

$$-13.6 = -5.71 \log k$$

$$\log k = \frac{-13.6}{-5.71} = 2.38$$

$$k = 10^{2.38} \text{ OR } k = 2.4\times10^2$$
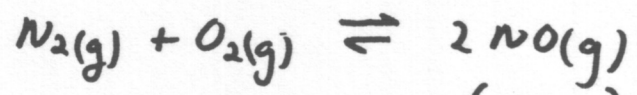
FIND THE VALUE OF K FOR THIS REACTION AT 2000°C.

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

1) FIND $\Delta S°$

$$191.5 + 205.0 \rightleftharpoons 2(210.6)$$

$$396.5 \rightleftharpoons 421.2$$

$$\Delta S° = 421.2 - 396.5 = 24.7 \text{ J/k}$$

2) FIND $\Delta H_F°$ $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$ (MAY BE LOOKED UP,)

$$0 + 0 \rightleftharpoons 2(90.3)$$

$$0 \rightleftharpoons 180.6$$

$$\Delta H_F° = 180.6 - 0 = 180.6 \text{ KJ}$$

3) SUBSTITUTE INTO $\Delta G° = \Delta H° - T\Delta S°$ GIBBS-HELMHOLTZ EQUATION

$$\Delta G° = 180.6 \text{ KJ} - \qquad (24.7)(2273°k)$$

$$= 180.6 - \qquad 56.1 \text{ KJ}$$

$$\Delta G° = 124.5 \quad \text{KJ AT 2000°C}$$

4) SOLVE FOR K

$$\Delta G° = -RT \times 2.303 \text{ LOG K}$$

$$\log K = \frac{-\Delta G°}{-8.31 \times 2273 \times 2.303}$$

$$\log K = \frac{-124.5 \text{ KJ}}{43.5 \text{ KJ}} = = -2.86$$

$$K = 10^{-2.86} = 1.4 \times 10^{-3}$$