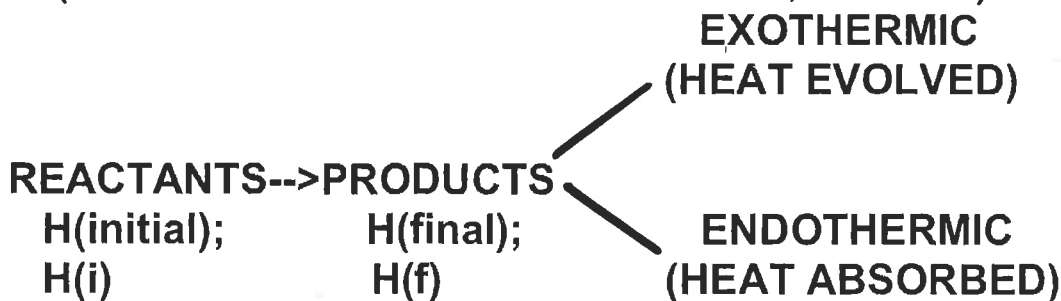


REVIEW OF EXO- AND ENDO-THERMIC REXNS

(STANDARD CONDITIONS ARE 25°C, 1 ATM P)



ENTHALPY CHANGE, $\Delta H = H(\text{final}) - H(\text{initial})$

EXOTHERMIC REXN
HEAT IS PRODUCED;
IF TEMP ISN'T HELD
CONSTANT BY REMOVING
HEAT, "- HEAT", TEMP OF
SYSTEM WILL INCREASE!

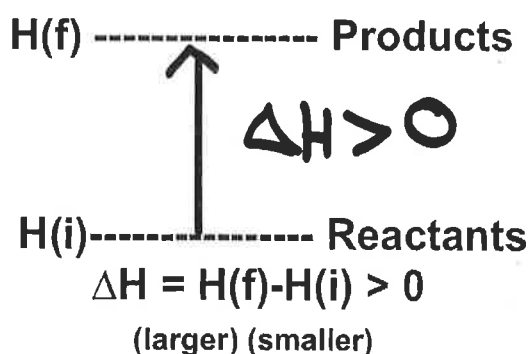
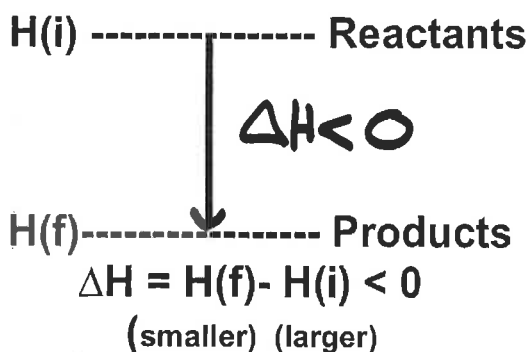
ENDOTHERMIC REXN
HEAT IS ABSORBED;
IF TEMP ISN'T HELD
CONSTANT BY ADDING
HEAT, "+ HEAT", SYSTEM
WILL COOL DOWN!

H, ENTHALPY (HEAT ENERGY) ↑

GRAPHICAL REPRESENTATIONS

EXOTHERMIC

ENDOTHERMIC



DEMO: DEHYDRATION OF
TABLE SUGAR, SUCROSE;

DEMO: STRONTIUM HYDROXIDE
ADDED TO AMMONIUM NITRATE;
AN ACID-BASE REXN

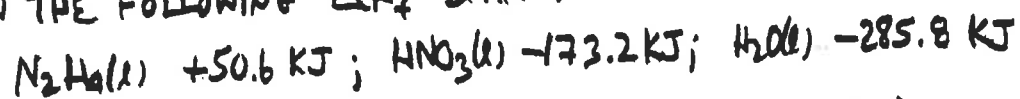
REALLY "COOL" DEMO!

SOME PROBLEMS IN THERMOCHEMISTRY

1. LIQUID HYDRAZINE, N_2H_4 , IS OXIDIZED BY NITRIC ACID ACCORDING TO THE FOLLOWING EQUATION:



GIVEN THE FOLLOWING ΔH_f° DATA:



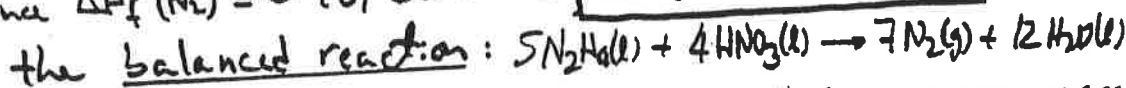
- CALCULATE ΔH° FOR THE ABOVE REACTION
 - DETERMINE ΔH° FOR THE OXIDATION OF 10.00 MOLES OF HYDRAZINE BY 9.00 MOLES OF NITRIC ACID.
 - DO THE SAME CALCULATION IN PART B IF 10.00 MOLES OF HYDRAZINE REACT WITH 6.000 MOLES OF NITRIC ACID
 - CALCULATE ΔH° FOR THE REACTION IN PART A IF 85.6 L OF N_2 GAS IS EVOLVED UNDER STANDARD THERMOCHEMICAL CONDITIONS.
2. A CALORIMETER CONTAINS 40.0 ml OF H_2O AT $40.0^\circ C$. ADDITION OF 10.0g OF ICE AT $0.0^\circ C$ TO THE CALORIMETER GIVES A FINAL TEMP. OF $20.0^\circ C$
GIVEN THE DATA: $\Delta H_{fusion}(ICE) = 6.009 \text{ KJ/mol}$;
 $C_{sp}(H_2O(l)) = 4.184 \text{ J g}^{-1} \text{ }^\circ C^{-1}$, DETERMINE THE CALORIMETER CONSTANT, C_{CAL} , IN UNITS OF $J^\circ C^{-1}$.
3. WHEN 0.364g OF Mg METAL WAS COMPLETELY BURNED TO GIVE $MgO(s)$ IN A CALORIMETER AT 1.000 ATM PRESSURE THE TEMPERATURE CHANGED FROM $23.68^\circ C$ TO $24.30^\circ C$ THE CALORIMETER CONSTANT WAS DETERMINED IN A SEPARATE EXPERIMENT TO BE $14.56 \text{ KJ}^\circ C^{-1}$.
CALCULATE THE ΔH_f° OF MgO .
4. ADDITION OF 1.00 ml OF CONCENTRATED SULFURIC ACID (DENSITY = 1.84 g cm^{-3}) TO 100 ml OF WATER CAUSED THE TEMPERATURE TO CHANGE FROM $22.0^\circ C$ TO $26.2^\circ C$. CALCULATE THE MOLAR HEAT OF SOLUTION OF H_2SO_4 IN H_2O . ASSUME $C_{CAL} = 0$

CHEM 1061-003 16 FEB 2015
 SOME PROBLEMS IN THERMOCHEMISTRY

ANSWERS

1. a. $\Delta H_{rxn} = 7\Delta H_f^\circ(N_2) + 12\Delta H_f^\circ(H_2O) - 5\Delta H_f^\circ(N_2H_4) - 4\Delta H_f^\circ(HNO_3)$

Since $\Delta H_f^\circ(N_2) = 0$ (By DEFINITION) $\Delta H_{rxn} = -2990 \text{ KJ}$ for



b. HYDRAZINE IS THE LIMITING REACTANT; HNO_3 IS PRESENT IN EXCESS.

THEREFORE THE AMOUNT OF HYDRAZINE ORIGINALLY PRESENT WILL DETERMINE

THE MAGNITUDE OF ΔH_{rxn} : $(10.00 \text{ mol } N_2H_4) \left(\frac{-2990 \text{ KJ}}{5 \text{ mol } N_2H_4} \right) = -5980 \text{ KJ}$

c. NITRIC ACID IS THE LIMITING REACTANT.

$\Delta H_{rxn} = (6.00 \text{ mol } HNO_3) \left(\frac{-2990 \text{ KJ}}{4 \text{ mol } HNO_3} \right) = -4485 \text{ KJ}$

d. $n_{N_2} = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(85.6 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm})(298 \text{ K})} = 3.50 \text{ mol } N_2$

$\Delta H_{rxn} = (3.50 \text{ mol } N_2) \left(\frac{-2990 \text{ KJ}}{7 \text{ mol } N_2} \right) = -1495 \text{ KJ}$

NOTE: STANDARD THERMOCHEMICAL CONDITIONS ARE 25°C , 1.00 atm .

2. $q_{\text{fusion}} + q_{\text{ice water}} + q_{\text{hot water}} + q_{\text{CAL}} = 0$;

$q_{\text{fusion}} = m(\text{ice}) \times \Delta H_{\text{fusion}}$; $q_{\text{ice water}} = (m_{\text{ice}}) C_{sp} \Delta T$; $\Delta T = T_f - T_i = 20.0^\circ\text{C}$

$q_{\text{HOT WATER}} = (m_{\text{hot water}}) (C_{sp}) (\Delta T')$; $q_{\text{CAL}} = C_{\text{CAL}} \Delta T'$; $\Delta T' = T_f - T_i = -20.0^\circ\text{C}$

$C_{\text{CAL}} = 41.2 \text{ J } ^\circ\text{C}^{-1}$

THIS PROBLEM WAS WORKED OUT ON 10/15/99

RELATED PROBLEM: (CALCULATE THE EXPECTED FINAL TEMP. OF THE WATER IN THE ABOVE SYSTEM (Q2) IF $C_{\text{CAL}} = 0$. ANSWER: 16.1°C)

3. $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ $\Delta H_{rxn} = -q_{\text{CAL}} = -C_{\text{CAL}} \Delta T$

$\Delta H_f^\circ MgO = \left(\frac{\Delta H_{rxn}}{0.346 \text{ g } Mg} \right) \left(\frac{24.31 \text{ g } Mg}{\text{mol } Mg} \right) \left(\frac{\text{mol } Mg}{\text{mol } MgO} \right) = -603 \text{ KJ}$ $\Delta H_{rxn} = \left(\frac{-14.56 \text{ KJ}}{0.62 \text{ g}} \right) (0.62 \text{ g})$

4. $q_{\text{rxn}} + q_{\text{dilute } H_2SO_4} + q_{\text{CAL}} = 0$ If $q_{\text{CAL}} = 0$,

$\Delta H_{rxn} = q_{\text{rxn}} = -q_{\text{dilute } H_2SO_4} = -(m_{\text{soln}}) (C_{sp}) (\Delta T)$

Assume C_{sp} equals that of pure H_2O : $\frac{4.184 \text{ J}}{g^\circ\text{C}}$

$m_{\text{soln}} = 100 \text{ g } H_2O + 1.8 \text{ g } H_2SO_4 = 101.8 \text{ g}$; $\Delta T = 4.2^\circ\text{C}$

$\Delta H_{rxn} = -(101.8 \text{ g soln}) \left(\frac{4.184 \text{ J}}{g^\circ\text{C}} \right) (4.2^\circ\text{C}) \left(\frac{\text{KJ}}{1000 \text{ J}} \right) = -1.79 \text{ KJ}$

Molar $\Delta H_{rxn} = \left(\frac{-1.79 \text{ KJ}}{1.84 \text{ g } H_2SO_4} \right) \left(\frac{98.08 \text{ g } H_2SO_4}{\text{mol } H_2SO_4} \right) = -95.4 \text{ KJ}$