

# HEAT CAPACITY CALCULATIONS

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THERE ARE ABOUT 100 MILLION SUCH WATER HEATERS IN THE US. IF ALL THE ENERGY IN ALL THOSE WATER HEATERS WERE TRANSFERRED AS HEAT TO THE EARTH ESTIMATE HOW MUCH THE TEMPERATURE RISE OF THE EARTH WOULD BE. NOTE: TABLE 10-1 PROVIDES ALL THE INFORMATION YOU NEED EXCEPT FOR THE MASS OF THE EARTH, WHICH IS  $6 \times 10^{24}$  kg.



# HEAT CAPACITY CALCULATIONS

## THE ANSWER

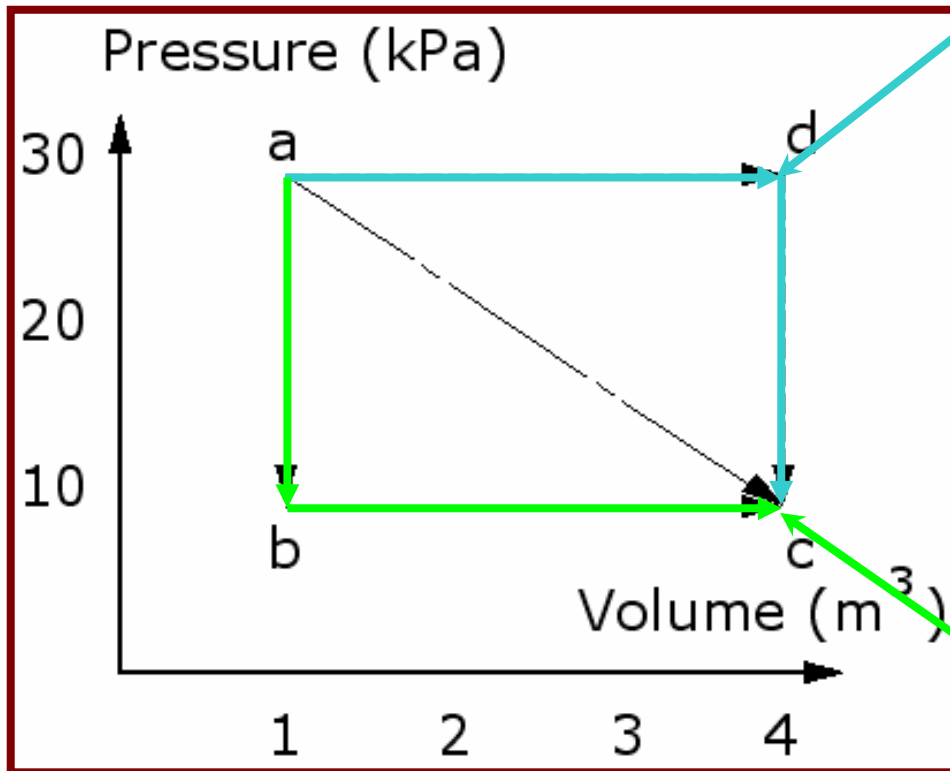
WE HAVE  $q = 6.3 \times 10^6$  cal PER WATER HEATER  
FOR  $10^8$  WATER HEATERS  $q = 6.3 \times 10^{14}$  cal

$$\begin{aligned}\Delta T_{\text{EARTH}} &= q / (m_{\text{EARTH}} \times C_{s,\text{EARTH}}) \\ &= (6.3 \times 10^{14} \text{ cal}) / [(6 \times 10^{27} \text{ g})(\approx 0.1 \text{ cal K}^{-1} \text{ g}^{-1})] \\ &\approx 1 \times 10^{-12} \text{ K}\end{aligned}$$

ESTIMATE FROM TABLE 10-1



# CALCULATION OF PV WORK



$$P_{\text{ext}} = 29 \text{ kPa}$$

$$\begin{aligned} W_{a-d-c} &= W_{a-d} \\ &= -P_{ad} \times (V_d - V_a) \\ &= -29 \text{ kPa} \times (4 - 1) \text{ m}^3 \\ &= -87 \text{ kJ} \end{aligned}$$

$$\begin{aligned} W_{a-b-c} &= W_{b-c} \\ &= -P_{bc} \times (V_c - V_b) \\ &= -9 \text{ kPa} \times (4 - 1) \text{ m}^3 \\ &= -27 \text{ kJ} \end{aligned}$$

$$P_{\text{ext}} = 9 \text{ kPa}$$



# CALCULATION OF PV WORK

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## CALCULATION OF PV WORK

IN THE EXAMPLE WE JUST CONSIDERED  
CALCULATE THE HEAT  $q$  FOR EACH STEP  
FOR A SYSTEM IN WHICH OXYGEN IS THE GAS,  
BEHAVING IDEALLY.



# CALCULATION OF PV WORK

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## THE ANSWER

THE SYSTEM HAS NOT BEEN DEFINED SUFFICIENTLY TO DO THIS CALCULATION, SINCE WE NEED TO SPECIFY THREE VARIABLES TO DEFINE THE STATE OF THE SYSTEM AND HERE WE HAVE SPECIFIED ONLY TWO. BUT, THE FIRST LAW ALLOWS YOU TO SAY THAT THE SUM OF THE WORK DONE AND THE HEAT ABSORBED MUST BE THE SAME FOR EACH PATH, SINCE THE INITIAL AND FINAL STATES OF THE SYSTEM ARE THE SAME FOR ALL THREE PATHS.



# CALCULATION OF PV WORK

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## CALCULATION OF PV WORK

YOUR 7-YEAR-OLD NEPHEW IS HAVING A BIRTHDAY PARTY. YOU ARE ASKED TO BLOW UP 75 BALLOONS. EACH BALLOON IS NO BIGGER THAN YOUR THUMB WHEN YOU START, BUT IS A SPHERE OF DIAMETER 25 CM WHEN INFLATED. HOW MUCH WORK WILL YOU PERFORM IN DOING THIS IF YOU ASSUME THAT THE BALLOON IS PERFECTLY ELASTIC?



# CALCULATION OF PV WORK

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## THE ANSWER

WHAT IS THE SYSTEM HERE? YOU ARE. SO, THE WORK,  $w$ , SHOULD BE NEGATIVE.

NOW  $w = -P \times \Delta V$  AS ALWAYS.

WE HAVE  $P = 1.01 \times 10^5 \text{ Pa}$  AND FOR EACH BALLOON  $\Delta V = \frac{4}{3} \pi r^3 = 8.2 \times 10^{-3} \text{ m}^3$ .

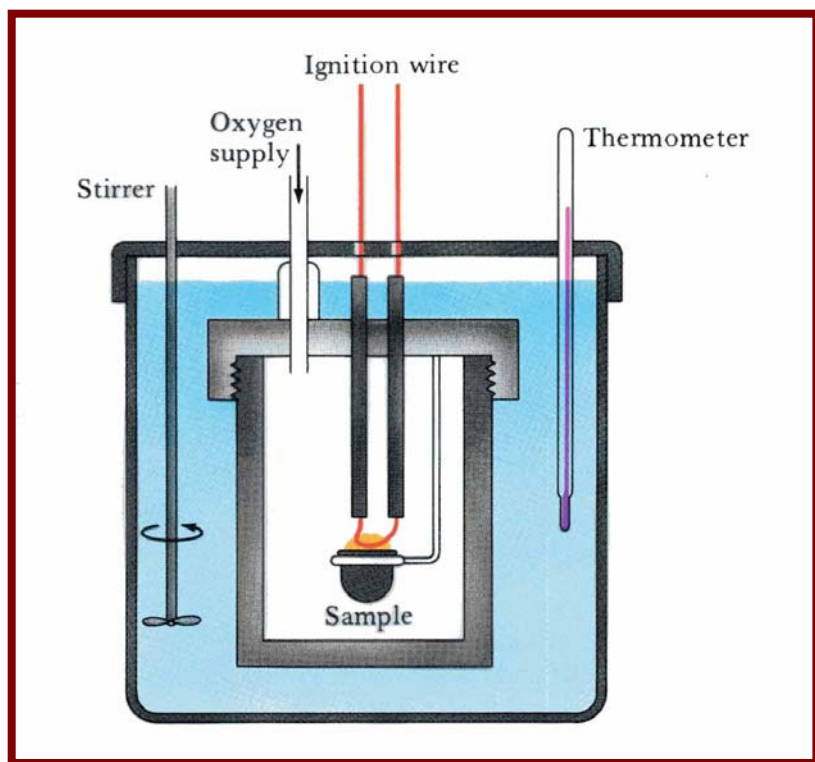
THE TOTAL WORK FOR 75 BALLOONS IS:

$$\begin{aligned} w &= - (1.01 \times 10^5 \text{ Pa}) \times (8.2 \times 10^{-3} \text{ m}^3) \times 75 \\ &= - 6.2 \times 10^4 \text{ J.} \end{aligned}$$



# CALORIMETRY

## THE CALORIMETER



WHAT DOES THE CALORIMETER MEASURE?  $\Delta T$

HOW IS THIS TEMPERATURE CHANGE RELATED TO  $q$ ?

$$q = m_{\text{calorimeter}} \times C_{s, \text{calorimeter}} \times \Delta T$$





# CALORIMETRY

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## WHAT DOES $q$ TELL US?

- ◆  $q$  IS NOT A STATE FUNCTION.  
IT IS PATH DEPENDENT.
- ◆ WE MUST CONNECT  $q$  TO A **STATE FUNCTION**.
- ◆ THE FIRST LAW ( **$\Delta E = q + w$** ) PROVIDES THE CONNECTION.



# CONSTANT VOLUME PROCESSES

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WHAT DOES  $q$  TELL US WHEN  $V$  IS CONSTANT?

THE FIRST LAW SAYS:  $\Delta E = q + w$ .

WHEN THE ONLY WORK POSSIBLE IS PV WORK AND  $V$  IS CONSTANT WE HAVE  $w = 0$ .

FOR ANY CONSTANT-VOLUME PROCESS UNDER CONDITIONS FOR WHICH ONLY PV WORK IS POSSIBLE  $\Delta E = q$ .



# CONSTANT PRESSURE PROCESSES

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WHAT DOES  $q$  TELL US WHEN  $P$  IS CONSTANT?

INTRODUCE A NEW STATE FUNCTION:

$$H = E + PV \text{ SO } \Delta H = \Delta E + \Delta(PV).$$

WHEN  $P$  IS CONSTANT  $\Delta H = \Delta E + (P \times \Delta V)$ .

WHEN ONLY  $PV$  WORK IS POSSIBLE

$$\Delta E = q + w = q - (P \times \Delta V),$$

$$\text{SO THEN } \Delta H = q - (P \times \Delta V) + (P \times \Delta V) = q.$$

FOR ANY CONSTANT-PRESSURE PROCESS UNDER CONDITIONS FOR WHICH ONLY  $PV$  WORK IS POSSIBLE  $\Delta H = q$ .



# CALORIMETRY

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CALORIMETRY IS THE EXPERIMENTAL BASIS  
OF THERMOCHEMISTRY

q CAN BE RELATED TO A STATE FUNCTION  
FOR BOTH CONSTANT-VOLUME AND  
CONSTANT-PRESSURE CONDITIONS.

CONSTANT-VOLUME PROCESSES TAKE PLACE  
IN A RIGID, CLOSED CONTAINER AND  $\Delta E = q$ .

CONSTANT-PRESSURE PROCESSES TAKE PLACE  
IN AN OPEN CONTAINER AND  $\Delta H = q$ .



# THERMOCHEMISTRY

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## CHEMICAL AND PHYSICAL CHANGE

- ◆ EVERY CHEMICAL TRANSFORMATION IS CHARACTERIZED BY PRECISE VALUES OF  $\Delta E$  AND  $\Delta H$ .
- ◆ EVERY PHYSICAL TRANSFORMATION IS CHARACTERIZED BY PRECISE VALUES OF  $\Delta E$  AND  $\Delta H$ .



# THERMOCHEMISTRY

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## COMPUTING $\Delta H$ AND $\Delta E$ FOR ANY REACTION

1. WRITE A BALANCED CHEMICAL REACTION, KEEPING TRACK OF PHYSICAL STATE.
2. RE-WRITE THIS REACTION AS A SUM OF STEPS TO MAKE USE OF AVAILABLE THERMOCHEMICAL DATA FOR  $\Delta H$  OR  $\Delta E$ .
3. ADD THE  $\Delta H$  OR  $\Delta E$  FOR ALL STEPS TO COMPUTE  $\Delta H$  OR  $\Delta E$  FOR THE REACTION.



# THERMOCHEMISTRY

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COMPUTING  $\Delta H$  AND  $\Delta E$  FOR ANY REACTION

THE MOST COMMONLY AVAILABLE  
THERMOCHEMICAL DATA ARE:

STANDARD ENTHALPY OF FORMATION

BOND ENTHALPY

STANDARD ENTHALPY OF PHASE CHANGE



# THE STANDARD STATE

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THERMOCHEMICAL CALCULATIONS  
ARE BASED ON THE STANDARD STATE

ENTHALPIES OF SUBSTANCES DEPEND ON  
TEMPERATURE, PRESSURE, AND PHYSICAL STATE.

THE STANDARD STATE IS USED TO PROVIDE A  
CONSISTENT BASIS FOR  $\Delta H$  CALCULATIONS.





# THE STANDARD STATE

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THERMOCHEMICAL CALCULATIONS  
ARE BASED ON THE STANDARD STATE

FOR SOLIDS AND LIQUIDS THE STANDARD STATE IS THE STATE OF THE PURE SOLID OR LIQUID UNDER A PRESSURE OF 1 ATMOSPHERE AT A STATED TEMPERATURE.

FOR GASES THE STANDARD STATE IS THE GASEOUS PHASE UNDER A PRESSURE OF 1 ATMOSPHERE AT A STATED TEMPERATURE.



# THE STANDARD STATE

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THERMOCHEMICAL CALCULATIONS  
ARE BASED ON THE STANDARD STATE

FOR DISSOLVED SPECIES THE STANDARD  
STATE IS THE STATE AT A CONCENTRATION  
OF  $1 \text{ mol}^{-1} \text{ L}^{-1}$  UNDER A PRESSURE OF 1  
ATMOSPHERE AT A STATED TEMPERATURE.



# THERMOCHEMICAL CALCULATIONS

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## THE THERMOCHEMISTRY OF TEFLON



# THERMOCHEMICAL CALCULATIONS

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## THE COMPOSITION OF TEFLON

TEFLON IS A POLYMER WITH THE FORMULA  $C_nF_{2n+2}$ , WHERE  $n$  IS SOME VERY LARGE NUMBER.

WE WILL USE  $C_3F_8$  AS A MODEL FOR TEFLON.



# THERMOCHEMICAL CALCULATIONS

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## THE THERMOCHEMISTRY OF TEFLON

WHY DOESN'T TEFLON BURN, THAT IS WHY DOESN'T IT REACT WITH OXYGEN?

THERMODYNAMICS HAS THE ANSWER.

THE ANSWER IS IN  $\Delta H_{\text{reaction}}$  ( $\Delta H_r$  FOR SHORT).

WHAT IS THIS THING  $\Delta H_r$ ?



# THERMOCHEMICAL CALCULATIONS

## THE REACTION OF TEFLON WITH OXYGEN

TEFLON + OXYGEN  $\rightarrow$  ?

TO COMPUTE  $\Delta H_r$  WE MUST FIRST WRITE  
A BALANCED CHEMICAL EQUATION.

FOR OUR MODEL OF TEFLON ( $C_3F_8$ ) THIS IS:



IT IS IMPERATIVE TO GIVE THE PHYSICAL STATE  
OF ALL REACTANTS AND PRODUCTS.



# THERMOCHEMICAL CALCULATIONS

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## THE STANDARD ENTHALPY OF FORMATION

TO COMPUTE  $\Delta H_r$  WE MUST THEN USE STANDARD THERMOCHEMICAL DATA.

HERE WE WILL USE  $\Delta H_f^\circ$ , THE STANDARD ENTHALPY OF FORMATION.

$\Delta H_f^\circ$ , THE STANDARD ENTHALPY OF FORMATION, IS THE ENTHALPY CHANGE FOR THE FORMATION OF A COMPOUND FROM ITS ELEMENTS IN THEIR STANDARD STATE.



# THERMOCHEMICAL CALCULATIONS

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## THE STANDARD ENTHALPY OF FORMATION

EXAMPLE: THE STANDARD ENTHALPY OF FORMATION FOR  $\text{C}_3\text{F}_8(\text{g})$  IS THE ENTHALPY CHANGE FOR THE REACTION:



WHICH IS  $\Delta H_f^\circ = -1,785 \text{ kJ mol}^{-1}$ .

EXAMPLE: THE STANDARD ENTHALPY OF FORMATION FOR  $\text{OF}_2(\text{g})$  IS THE ENTHALPY CHANGE FOR THE REACTION:



WHICH IS  $\Delta H_f^\circ = 25 \text{ kJ mol}^{-1}$ .





# THERMOCHEMICAL CALCULATIONS

USING THE STANDARD ENTHALPY OF FORMATION

FOR THE REACTION:  $aA + bB \rightarrow cC + dD$

$$\Delta H_r = c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D) - a\Delta H_f^\circ(A) - b\Delta H_f^\circ(B)$$

FOR THE REACTION:

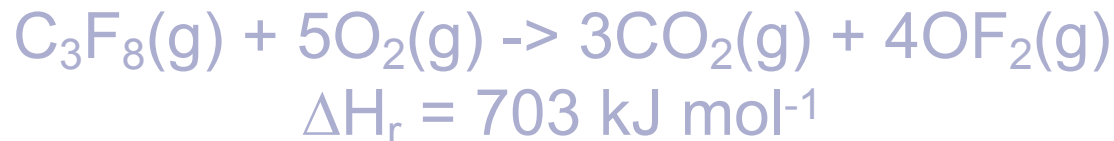


$$\begin{aligned}\Delta H_r &= 3\Delta H_f^\circ(CO_2(g)) + 4\Delta H_f^\circ(OF_2(g)) \\ &\quad - 1\Delta H_f^\circ(C_3F_8(g)) - 5\Delta H_f^\circ(O_2(g)) \\ &= 3(-394 \text{ kJ mol}^{-1}) + 4(25 \text{ kJ mol}^{-1}) \\ &\quad - (-1,785 \text{ kJ mol}^{-1}) - 5(0 \text{ kJ mol}^{-1}) \\ &= 703 \text{ kJ mol}^{-1}\end{aligned}$$



# THERMOCHEMICAL CALCULATIONS

## THE IMPLICATION OF THIS RESULT



THIS LARGE POSITIVE VALUE OF  $\Delta H_r$  MEANS THAT THE REACTION IS HIGHLY **ENDOTHERMIC** AND WILL NOT OCCUR WITHOUT THE ADDITION OF A GREAT DEAL OF HEAT TO THE SYSTEM. REACTION WILL ONLY OCCUR AT VERY HIGH TEMPERATURE, SO TEFLON WILL NOT REACT READILY WITH OXYGEN EVEN AT THE TEMPERATURES OF A COOKING PAN.



# THERMOCHEMICAL CALCULATIONS

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## THE REACTION OF TEFLON

WILL TEFLON NOT REACT WITH ANYTHING AT ALL? USE THE  $\Delta H_f^\circ$  DATA IN APPENDIX D OF YOUR TEXT TO FIND SOMETHING WITH WHICH TEFLON WILL REACT READILY. THAT IS, FIND A REACTION OF TEFLON WITH SOMETHING THAT WILL GIVE A  $\Delta H_r$  THAT IS LARGE AND NEGATIVE.

ANSWER TOMORROW.



# THERMOCHEMICAL CALCULATIONS

## THE SPACE SHUTTLE ENGINES



SOLID ROCKET BOOSTERS

MAIN ENGINES



# THERMOCHEMISTRY

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## THE SPACE SHUTTLE MAIN ENGINES

THE SPACE SHUTTLE MAIN ENGINES OPERATE ON THE REACTION OF HYDROGEN WITH OXYGEN.

THE HYDROGEN AND OXYGEN ARE CARRIED AS LIQUIDS AT THEIR BOILING POINTS.

THE OVERALL REACTION IS:



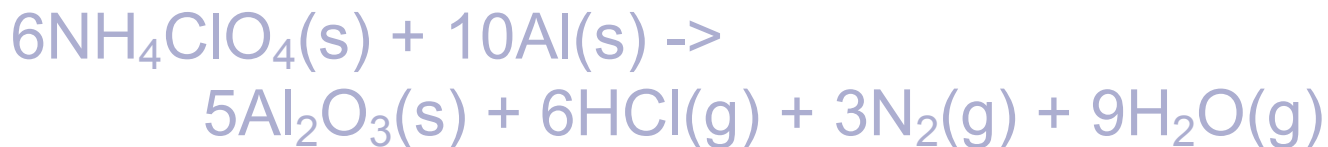
# THERMOCHEMISTRY

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## THE SPACE SHUTTLE SOLID ROCKET BOOSTERS

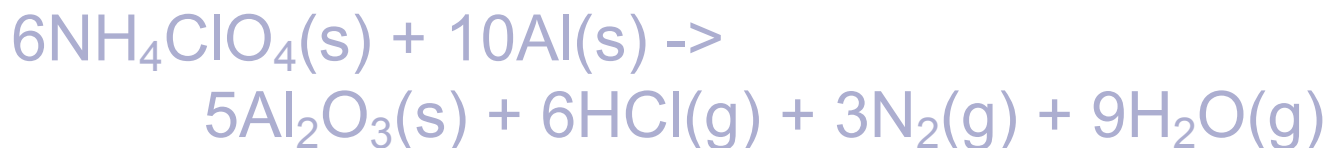
THE SPACE SHUTTLE SOLID ROCKET BOOSTERS OPERATE ON THE REACTION OF AMMONIUM PERCHLORATE WITH ALUMINUM.

THE OVERALL REACTION IS:



# THERMOCHEMISTRY

## THE SPACE SHUTTLE SOLID ROCKET BOOSTERS



$$\begin{aligned}\Delta H_r &= 5\Delta H_f^\circ(\text{Al}_2\text{O}_3(\text{s})) + 6\Delta H_f^\circ(\text{HCl}(\text{g})) + \\ &\quad 3\Delta H_f^\circ(\text{N}_2(\text{g})) + 9\Delta H_f^\circ(\text{H}_2\text{O}(\text{g})) \\ &\quad - 6\Delta H_f^\circ(\text{NH}_4\text{ClO}_4(\text{s})) - 10\Delta H_f^\circ(\text{Al}(\text{s})) \\ &= 5[-1,676 \text{ kJ mol}^{-1}] + 6[-92 \text{ kJ mol}^{-1}] + \\ &\quad 3[0 \text{ kJ mol}^{-1}] + 9[-242 \text{ kJ mol}^{-1}] \\ &\quad - 6[-296 \text{ kJ mol}^{-1}] - 10[0 \text{ kJ mol}^{-1}] \\ &= -9,334 \text{ kJ mol}^{-1} \text{ OF REACTION AS WRITTEN}\end{aligned}$$



# THERMOCHEMISTRY

## INTERPRETTING $\Delta H_r$

$\Delta H_r = -9,334$  kJ PER MOLE OF REACTION AS WRITTEN.

THIS MEANS 9,334 kJ OF ENERGY ARE RELEASED WHEN **6** MOLES OF  $\text{NH}_4\text{ClO}_4(\text{s})$  REACT WITH **10** MOLES OF  $\text{Al}(\text{s})$  TO GIVE **5** MOLES OF  $\text{Al}_2\text{O}_3(\text{s})$  AND **6** MOLES OF  $\text{HCl}(\text{g})$  AND **3** MOLES OF  $\text{N}_2(\text{g})$  AND **9** MOLES OF  $\text{H}_2\text{O}(\text{g})$ .

SO,

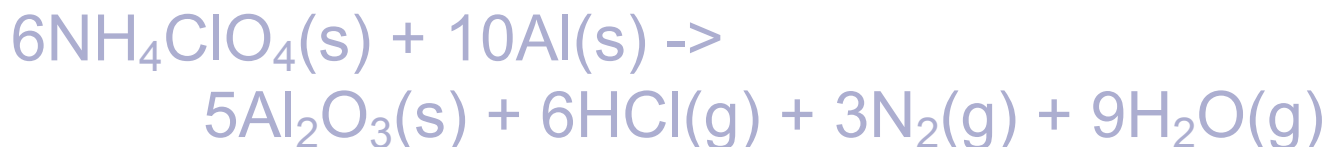
$\Delta H_r = (-9,334/6)$  kJ PER MOLE OF  $\text{NH}_4\text{ClO}_4$  CONSUMED  
=  $(-9,334/10)$  kJ PER MOLE OF  $\text{Al}$  CONSUMED  
=  $(-9,334/5)$  kJ PER MOLE OF  $\text{Al}_2\text{O}_3$  PRODUCED  
=  $(-9,334/6)$  kJ PER MOLE OF  $\text{HCl}$  PRODUCED  
AND SO FORTH.





# THERMOCHEMISTRY

## INTERPRETTING $\Delta H_r$



$$\Delta H_r = -9,334 \text{ kJ mol}^{-1}$$

THIS REACTION HAS A LARGE NEGATIVE VALUE OF  $\Delta H_r$ , WHICH MEANS THAT IT IS VERY **EXOTHERMIC**. IT RELEASES A LARGE AMOUNT OF HEAT AND OCCURS SPONTANEOUSLY.



# THERMOCHEMISTRY

## A CLOSER LOOK AT THIS REACTION

THE LARGE EXOTHERMICITY IS DUE ALMOST ENTIRELY TO THE LARGE NEGATIVE HEAT OF FORMATION OF  $\text{Al}_2\text{O}_3$ . WHAT IS  $\text{Al}_2\text{O}_3$ ?

