HEAT CAPACITY CALCULATIONS

THERE ARE ABOUT 1OO 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 X 10^{24} kg.

HEAT CAPACITY CALCULATIONS

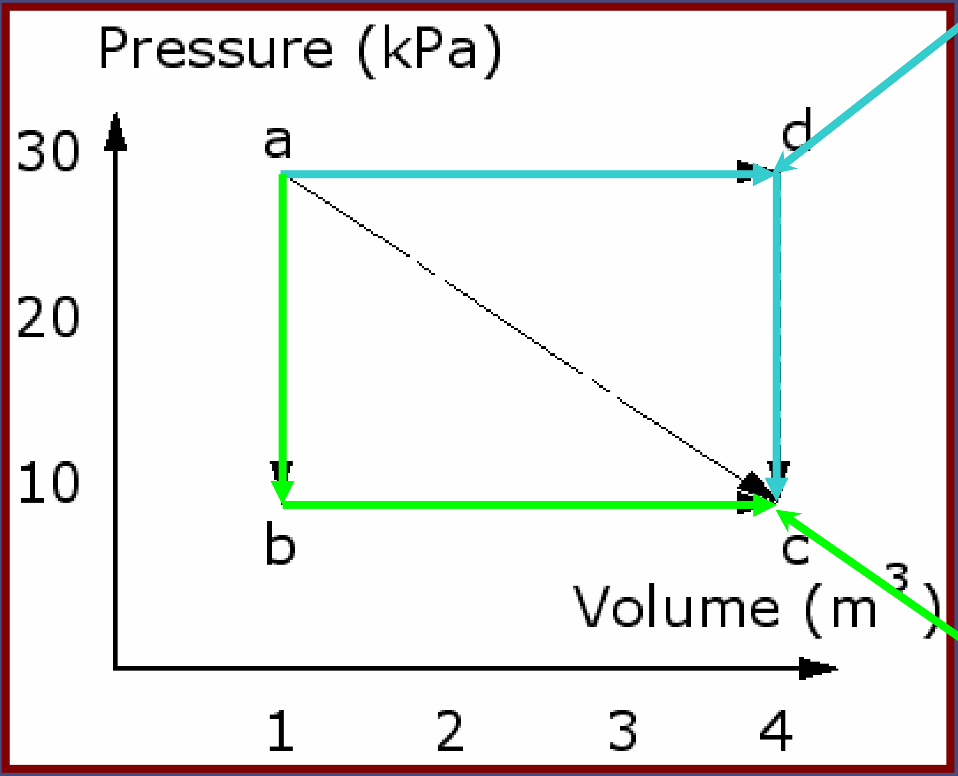
THE ANSWER

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

$$\Delta T_{\mathrm{EARTH}} = q/(m_{\mathrm{EARTH}} \times c_{\mathrm{s,EARTH}})$$
$$= (6.3 \times 10^{14}\ \mathrm{cal})/[(6 \times 10^{27}\ \mathrm{g})(\approx 0.\ 1\ \mathrm{cal\ K^{-1}\ g^{-1}})]$$
$$\approx 1 \times 10^{-12}\ \mathrm{K}$$

ESTIMATE FROM TABLE 10-1

CALCULATION OF PV WORK



P_{ext} = 29 kPa

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

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

P_{ext} = 9 kPa

CALCULATION OF PV WORK

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

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

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?

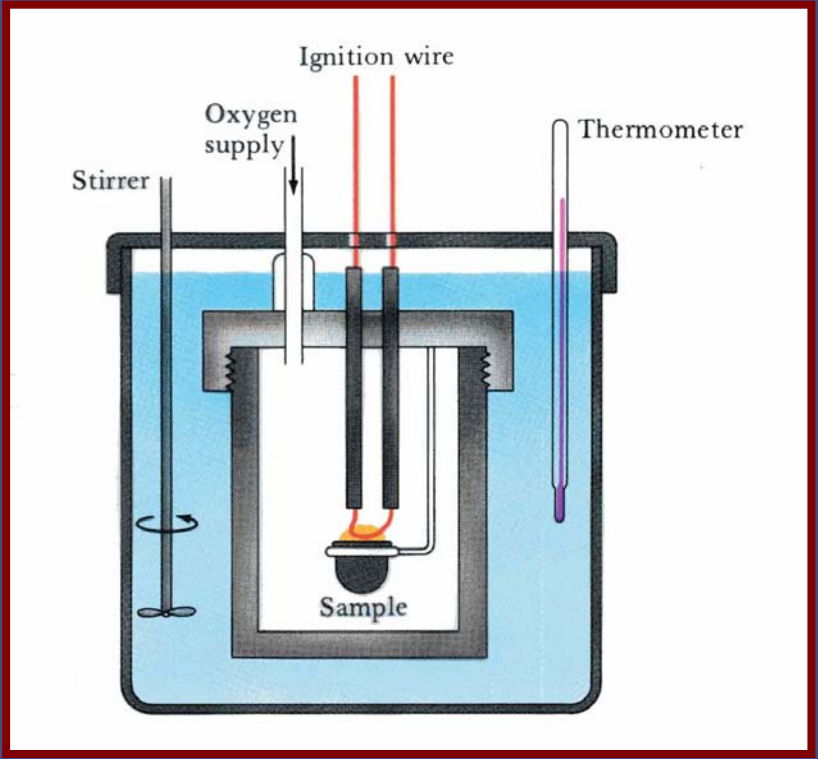
CALCULATION OF PV WORK

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 $P = 1.01 \times 10^5$ Pa AND FOR EACH BALLOON $\Delta V = 4/3\ \pi\ r^3 = 8.2 \times 10^{-3}\ m^3$.
THE TOTAL WORK FOR 75 BALLOONS IS:
$w = - (1.01 \times 10^5\ Pa) \times (8.2 \times 10^{-3}\ m^3) \times 75$
$= - 6.2 \times 10^4\ J$.

CALORIMETRY

THE CALORIMETER



WHAT DOES THE CALORIMETER MEASURE? ΔT

HOW IS THIS TEMPERATURE CHANGE RELATED TO q?

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

CALORIMETRY

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

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

WHAT DOES q TELL US WHEN P IS CONSTANT?

INTRODUCE A NEW STATE FUNCTION:
$H = E + PV$ 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
$\Delta E = q + w = q - (P \times \Delta V)$,
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

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 RIDID, CLOSED CONTAINER AND $\Delta E = q$.

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

THERMOCHEMISTRY

CHEMICAL AND PHYSICAL CHANGE

- EVERY CHEMICAL TRANSFORMATION IS CHARACTERIZED BY PRECISE VALUES OF ΔE AND ΔH.
- EVERY PHYSICAL TRANSFORMATION IS CHARACTERIZED BY PRECISE VALUES OF ΔE AND ΔH.

THERMOCHEMISTRY

COMPUTING ΔH AND ΔE 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 ΔH OR ΔE.
3. ADD THE ΔH OR ΔE FOR ALL STEPS TO COMPUTE ΔH OR ΔE FOR THE REACTION.

THERMOCHEMISTRY

COMPUTING ΔH AND ΔE FOR ANY REACTION

THE MOST COMMONLY AVAILABLE THERMOCHEMICAL DATA ARE:

STANDARD ENTHALPY OF FORMATION

BOND ENTHALPY

STANDARD ENTHALPY OF PHASE CHANGE

THE STANDARD STATE

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 ΔH CALCULATIONS.

THE STANDARD STATE

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

THERMOCHEMICAL CALCULATIONS
ARE BASED ON THE STANDARD STATE

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

THERMOCHEMICAL CALCULATIONS

THE THERMOCHEMISTRY OF TEFLON

THERMOCHEMICAL CALCULATIONS

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

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 $\Delta H_{reaction}$ (ΔH_r FOR SHORT).

WHAT IS THIS THING ΔH_r?

THERMOCHEMICAL CALCULATIONS

THE REACTION OF TEFLON WITH OXYGEN

TEFLON + OXYGEN -> ?

TO COMPUTE ΔH_r WE MUST FIRST WRITE A BALANCED CHEMICAL EQUATION.

FOR OUR MODEL OF TEFLON (C_3F_8) THIS IS:
$C_3F_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4OF_2(g)$

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

THERMOCHEMICAL CALCULATIONS

THE STANDARD ENTHALPY OF FORMATION

TO COMPUTE ΔH_r WE MUST THEN USE STANDARD THERMOCHEMICAL DATA.

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

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

THERMOCHEMICAL CALCULATIONS

THE STANDARD ENTHALPY OF FORMATION

EXAMPLE: THE STANDARD ENTHALPY OF FORMATION FOR $C_3F_8(g)$ IS THE ENTHALPY CHANGE FOR THE REACTION:

$$3C(s) + 4F_2(g) \rightarrow C_3F_8(g)$$

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

EXAMPLE: THE STANDARD ENTHALPY OF FORMATION FOR $OF_2(g)$ IS THE ENTHALPY CHANGE FOR THE REACTION:

$$1/2O_2(g) + F_2(g) \rightarrow OF_2(g)$$

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

THERMOCHEMICAL CALCULATIONS

USING THE STANDARD ENTHALPY OF FORMATION

FOR THE REACTION: aA + bB -> cC + dD

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

FOR THE REACTION:

$$C_3F_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4OF_2(g)$$

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

THERMOCHEMICAL CALCULATIONS

THE IMPLICATION OF THIS RESULT

$$C_3F_8(g) + 5O_2(g) -> 3CO_2(g) + 4OF_2(g)$$

$$\Delta H_r = 703 \text{ kJ mol}^{-1}$$

THIS LARGE POSITIVE VALUE OF ΔH_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

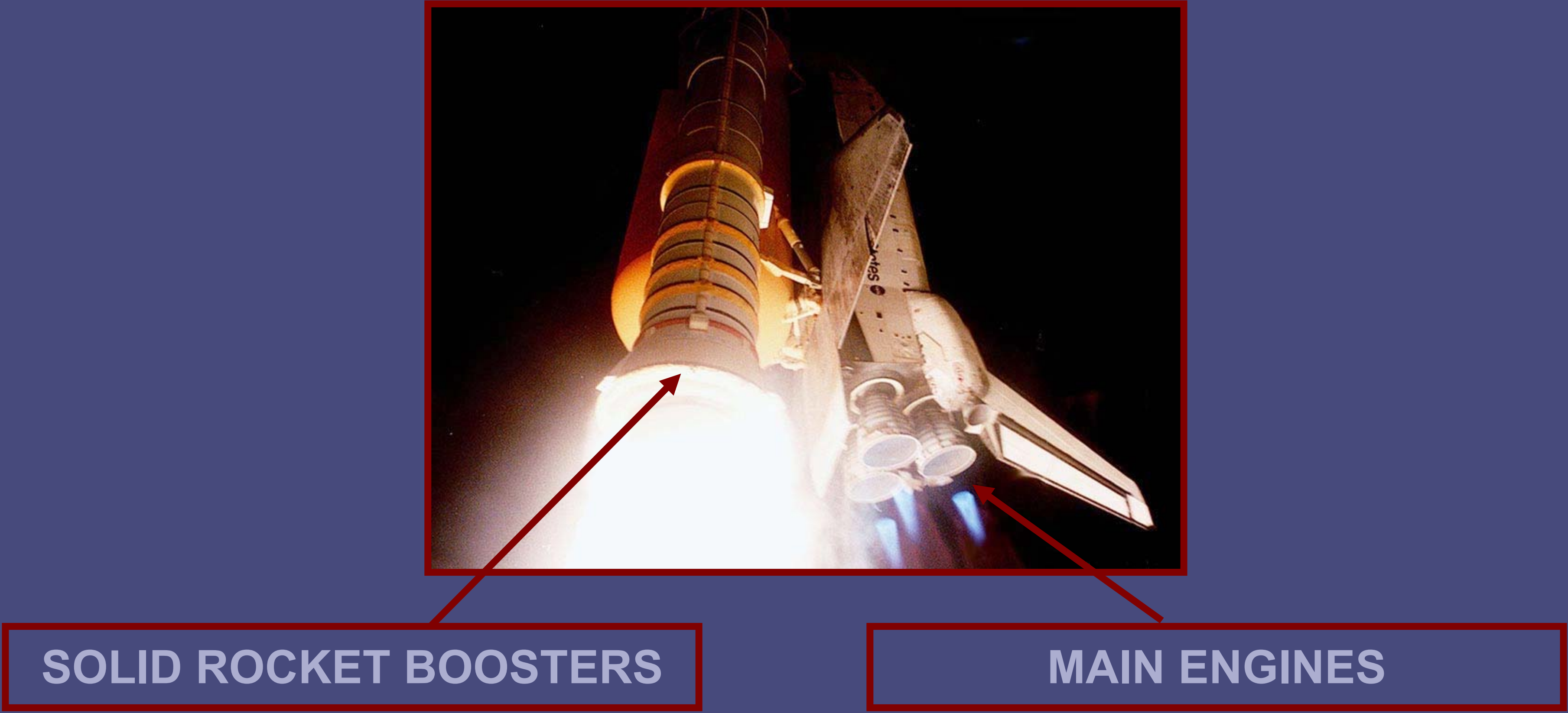
THE REACTION OF TEFLON

WILL TEFLON NOT REACT WITH ANYTHING AT ALL? USE THE $\Delta H_f°$ 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 ΔH_r THAT IS LARGE AND NEGATIVE.

ANSWER TOMORROW.

THERMOCHEMICAL CALCULATIONS

THE SPACE SHUTTLE ENGINES



SOLID ROCKET BOOSTERS

MAIN ENGINES

THERMOCHEMISTRY

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:
$2H_2(l) + O_2(l) \rightarrow 2H_2O(g)$

THERMOCHEMISTRY

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:
$6NH_4ClO_4(s) + 10Al(s) \rightarrow$
$5Al_2O_3(s) + 6HCl(g) + 3N_2(g) + 9H_2O(g)$

THERMOCHEMISTRY

THE SPACE SHUTTLE SOLID ROCKET BOOSTERS

$6NH_4ClO_4(s) + 10Al(s) ->$
$5Al_2O_3(s) + 6HCl(g) + 3N_2(g) + 9H_2O(g)$

$\Delta H_r = 5\Delta H_f°(Al_2O_3(s)) + 6\Delta H_f°(HCl(g)) +$
$3\Delta H_f°(N_2(g)) + 9\Delta H_f°(H_2O(g))$
$- 6\Delta H_f°(NH_4ClO_4(s)) - 10\Delta H_f°(Al(s))$
$= 5[-1,676 \text{ kJ mol}^{-1}] + 6[-92 \text{ kJ mol}^{-1}] +$
$3[0 \text{ kJ mol}^{-1}] + 9[-242 \text{ kJ mol}^{-1}]$
$- 6[-296 \text{ kJ mol}^{-1}] - 10[0 \text{ kJ mol}^{-1}]$
$= -9,334 \text{ kJ mol}^{-1}$ OF REACTION AS WRITTEN

THERMOCHEMISTRY

INTERPRETTING ΔH_r

ΔH_r = -9,334 kJ PER MOLE OF REACTION AS WRITTEN.

THIS MEANS 9,334 kJ OF ENERGY ARE RELEASED WHEN 6 MOLES OF $NH_4ClO_4(s)$ REACT WITH 10 MOLES OF Al(s) TO GIVE 5 MOLES OF $Al_2O_3(s)$ AND 6 MOLES OF HCl(g) AND 3 MOLES OF $N_2(g)$ AND 9 MOLES OF $H_2O(g)$.

SO,

ΔH_r = (-9,334/6) kJ PER MOLE OF NH_4ClO_4 CONSUMED
= (-9,334/10) kJ PER MOLE OF Al CONSUMED
= (-9,334/5) kJ PER MOLE OF Al_2O_3 PRODUCED
= (-9,334/6) kJ PER MOLE OF HCl PRODUCED
AND SO FORTH.

THERMOCHEMISTRY

INTERPRETTING ΔH_r

$$6NH_4ClO_4(s) + 10Al(s) \rightarrow 5Al_2O_3(s) + 6HCl(g) + 3N_2(g) + 9H_2O(g)$$

ΔH_r = -9,334 kJ mol-1

THIS REACTION HAS A LARGE NEGATIVE VALUE OF ΔH_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 Al_2O_3. WHAT IS Al_2O_3?