

TABLES ~Bond Energy ~Bond Length

Bond Energies (kJ/mol)

Bond Energy
436
415
390
464
569
395
320

-	
Bond	Bond Energy
C-S	260
C-CI	330
C-Br	275
C-I	240
N-N	160
$\mathbf{N} = \mathbf{N}$	418
$N \equiv N$	946

Bond	Bond Energy
F-CI	255
F-Br	235
Si-Si	230
Si-P	215
Si-S	225
Si-Cl	359
Si–Br	290

Table 7.2

		Bond Ene	ergies (kJ/mol)		
Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H-S	340	N–O	200	Si-I	215
H-CI	432	N-F	270	P-P	215
H-Br	370	N-P	210	P-S	230
H-I	295	N-CI	200	P-CI	330
C-C	345	N–Br	245	P-Br	270
C = C	611	0-0	140	P-I	215
C≡C	837	0=0	<mark>4</mark> 98	S-S	215
C-N	290	0-F	160	S-CI	250
C = N	615	O-Si	370	S-Br	215
$C \equiv N$	891	0-P	350	CI-CI	243
C-0	350	O-CI	205	CI-Br	220
C = O	741	0-I	200	CI-I	210
C≡O	1080	F-F	160	Br-Br	190
C-F	439	F-Si	540	Br-I	180
C-Si	360	F-P	489	I-I	150
C-P	265	F-S	285		

Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C-C	1.54	345
C = C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C = N	1.38	615
$C \equiv N$	1.16	891
C-0	1.43	350
C = O	1.23	741
$C \equiv O$	1.13	1080

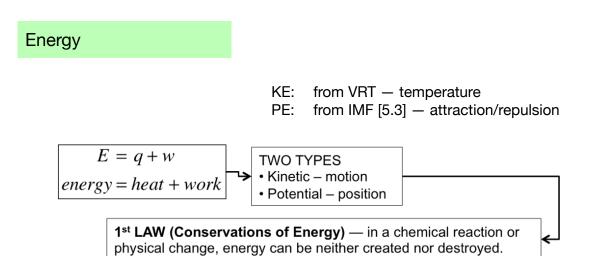
Table 7.3

Table 7.2

CHAPTER 5 THERMOCHEMISTRY

Energy Basics [5.1]

- Thermochemistry -- aka Chemical Thermodynamics -- heat & energy flow
- Chemistry is the study of matter: it's properties, interactions, reactions, and ENERGY CHANGES.
- $\bullet\,\Delta E$ occurs with almost every chemical, physical, or nuclear change



Thermal Energy, Temperature, and Heat

THERMAL ENERGY MANEFESTS as three types of molecular/atomic motion:

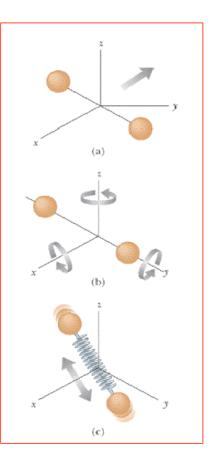
- 1 Vibrational
- 2 Rotational
- ③ Translational

RELATIONSHIP: TEMPERATURE AND MOTION

- → T_{\sim} amount of motions \blacksquare more motion = higher temp
- ►> T ~ KE(AVERAGE)

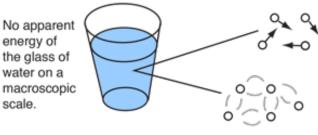
RELATIONSHIP: MATTER AND MOTION

- · Gas motion such that molecules cannot interact
- · Liquid motion such that molecules can interact somewhat
- solid motion such that molecules interact significantly



KE (VRT)

Does a glass of water sitting on a table have any energy?



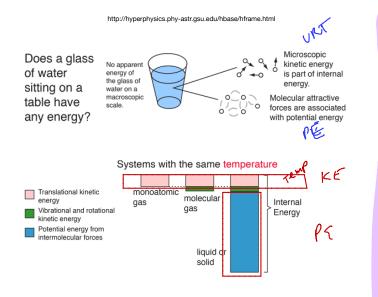
Microscopic kinetic energy is part of internal energy.

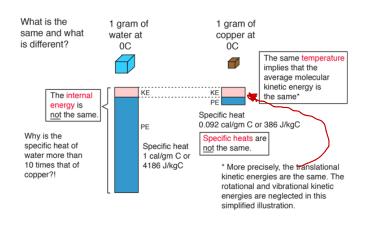
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Molecular attractive forces are associated with potential energy

PE (bonding)

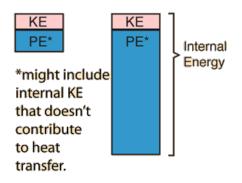
↓ ASIDE ↓





SPRCIME INAT

Temperature is not directly proportional to internal energy since temperature measures only the kinetic energy part of the internal energy, so two objects with the same temperature do not in general have the same internal energy



http://chemsite.lsrhs.net/chemKinetics/PotentialEnergy.html

Chemical Potential Energy A chemical bond can be thought of as an attractive force between atoms. Because of this, atoms and molecules can have chemical potential energy.

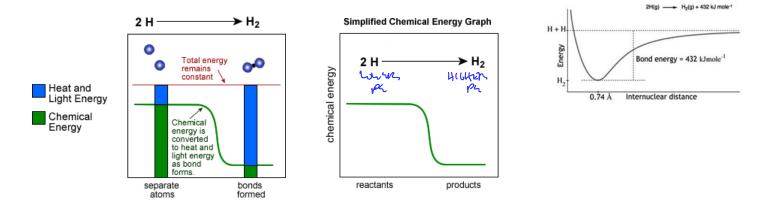
Anytime two atoms form a strong covalent or ionic bond or two molecules form a weak van der Waals bond, chemical energy is converted into other forms of energy, usually in the form of heat and light.

-> The amount of energy in a bond is somewhat counterintuitive - the stronger or more stable the bond, the less chemical energy there is between the bonded atoms.

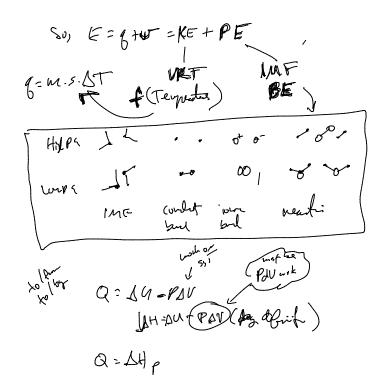
Strong bonds have low chemical energy and weak bonds have high chemical energy.

Lot's of heat and/or light energy is released when very strong bonds form, because much of the chemical energy is converted to heat and/or light energy. The reverse is true for breaking chemical bonds. It takes more energy to break a strong bond than a weak bond. The breaking of a bond requires the absorption of heat and/or light energy which is converted into chemical energy when the bond is broken.

See an example below of how a chemical reaction converts chemical energy into heat and light energy:



http://chemsite.lsrhs.net/chemKinetics/PotentialEnergy.html



http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/firlaw.html#c1

An increase in the enthalpy H = U + PV might be associated with an increase in internal energy which could be measured by calorimetry, or with work done by the system, or a combination of the two.

The internal energy U might be thought of as the energy required to create a system in the absence of changes in temperature or volume.

But if the process changes the volume, as in a chemical reaction which produces a gaseous product, then work must be done to produce the change in volume. For a constant pressure process the work you must do to produce a volume change ΔV is P ΔV . Then the term PV can be interpreted as the work you must do to "create room" for the system if you presume it started at zero volume.

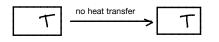
1 ASIDE 1

Heat

• HEAT (q), or heat flow, is the transfer of thermal energy between two bodies at different temperatures.

AT	heat transfer	LT

• THERMAL EQUILIBRIUM -- both substances are at the same temperature, and their molecules have the same average kinetic energy.



@ equil: KE(object 1) = KE(object 1)

E LIT LAW ENDO vs. EXO LIVIS Hope UMVERS 2 **SURROUNDINGS** SYSTEM exo cooler · → warmer endo cooler warmer

SYS + 2 MKR - UNIVERSE

Units of Measure

- >> A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin).
- ➤ The Calorie (with a capital C), is commonly used in quantifying food energy content, is a kilocalorie.

 \hookrightarrow is also known as a "large calorie", or "food calorie,"

for example, an apple contains about 90 Cal (which is 90 Kcal, or 90,000 cal)

- ➤ The SI unit of heat, work, and energy is the joule.
 ↓ A joule (J) is the amount of energy used when a force of 1 newton moves an object 1 meter.
 ↓ One joule is equivalent to 1 kg m 2 /s 2, which is also called 1 newton-meter.
- \rightarrow 1 calorie is equal to 4.184 joules.
- ►> Two useful conversion factors:

 $\left(\frac{4.1845}{cal}\right)$ $\left(\frac{1000 cal}{C}\right)$

HEAT CAPACITY

- · [def] the amt of heat absorbed or released when undergoing a temperature change
- Extensive property (dependent on AMOUNT of material present)

$$C = \frac{q}{\Delta T} \left(\frac{J}{^{o}C}\right) \qquad \text{Heat Capacity (C)}$$

SPECIFIC HEAT CAPACITY ("SPECIFIC HEAT")

- [def] the amt of heat needed to raise 1 g of material 1°C (or K)
- Intensive property (depends on the KIND material present)

$$c = \frac{q}{m\Delta T} \quad \left(\frac{J}{g^{\circ}C}\right)$$

MISC VALUES • 4.148 - water • 2.093 – ice • 1.864 – steam • 1.007 – air • 0.897 – Al • 0.449 - Fe Specific heat capacity (x) → .0.385 – Cu .0.130 – Pb • 0.129 – Au

Heat calculations

$$q = m s \Delta T \quad (J)$$
how much \Box how far
how hard

(EX) Calculate Heat for Given Temperature Change ¿How much heat, in J, is needed to raise 205 g of water from 21.2 °C to 94.4 °C? [ex 1-20; w10]

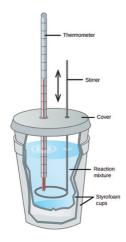
?
$$J = \frac{205g}{1} \cdot \frac{4.18J}{1g \cdot {}^{\circ}C} \cdot \frac{79.2 \,{}^{\circ}C}{1} = 6.02 \times 10^4 J$$

 $\cdot \frac{1kJ}{1000J} = 6.02 kJ$
 $q = m$ s ΔT

Calorimetry [5.2]

CALORIMETRY — "calor" = heat; metry = "measure" Calorimeter -- device to measure Q chg

SYSTEM	exo		- SolyTION
warmer «	endo	cooler	

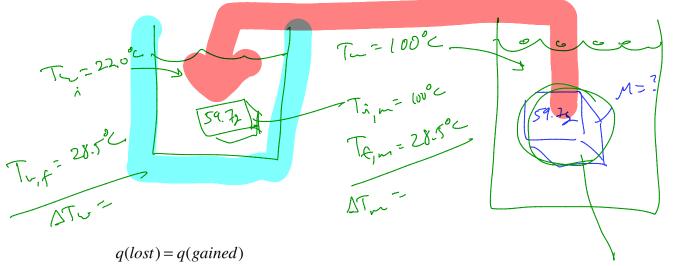


Fundamental Calorimetry Equations

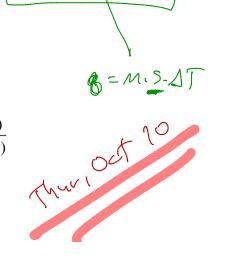
 $(k) \quad q(in) = q(out)$ q(lost) = q(gained) $\Sigma q_{(items that \ LOSE \ heat)} = \Sigma q_{(items \ that \ GAIN \ heat)}$

(EX) ID Metal via Calorimetry [ex 5.4]

¿A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to ID the metal?



q(lost) = -q(gained by water) q(lost by metal) = -q(gained by water) $m_M s_M \Delta T_M = m_W s_W \Delta T_W$ $s_M = \frac{m_W s_W \Delta T_W}{m_M \Delta T_M} = \frac{-60.0g}{59.7g} \frac{4.184J}{g^{\circ}C} \frac{(28.5^{\circ}C - 22.0^{\circ}C)}{(28.5^{\circ}C - 100.0^{\circ}C)}$ $s_M = 0.35J / g^{\circ}C$ - > this value is very probably copper



(EX) Calc heat produced by RXN [ex 5.5b] ¿When 100. m) of 0.200 M NaCl(aq) and 100. m) of 0.200 M AgNO3(aq), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCI forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value? KN M. S. J в юн - в саша в. 1 - в нат Стала - в гоза $\frac{1}{1} = \frac{1}{2} \frac{$ LOME - CUTO NEW - Oca

(EX) Calc heat produced by RXN [ex 5.5b] ;When 100. mL of 0.200 M NaCl(aq) and 100. mL of 0.200 M AgNO3(aq), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

q(lost) = q(gained) q(lost by chemial rxn) = -[q(gained by solution) + q(gained by calorimeter)] -> assume no heat absorbed by calorimeter q(rxn) = q(solution) -> assume solution has same specific heat as water -> assume solution has same density as water $q(rxn) = ms \Delta T = \frac{(100g + 100g)}{g^{\circ}C} \frac{4.184J}{g^{\circ}C} \frac{(23.5 - 21.9^{\circ}C)}{g^{\circ}C}$ $q(rxn) = 1338J \implies 1340J$

Bomb Calorimetry

SEALED... used to det'n Heats of Reaction

 \hookrightarrow can produce large pressure, hence the term "bomb"

(EX) Calc heat of combustion [ex 5.7b]

¿When 0.963 g of benzene, C6H6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glugges sample?

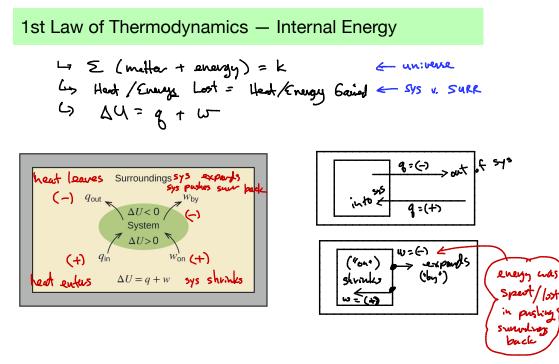
benjere 9256 = m.r. AT 924 PLOST = BCAINED ERON = 9SURN = P cal = CAT 2 72 ∆-8.3 q(lost by chemial rxn) = -[q(gained by solution) + q(gained by calorimeter)]-> assume solution has same specific heat as water 2

-> assume solution has same density as water

$$q(rxn) = ms \Delta T = \left[\frac{925g}{g^{\circ}C} \cdot \frac{4.184J}{g^{\circ}C} \cdot \frac{8.39^{\circ}C}{g^{\circ}C}\right] + \left[\frac{784J}{G^{\circ}C} \cdot \frac{8.39^{\circ}C}{g^{\circ}C}\right]$$
$$q(rxn) = 39,048J \implies 39.0kJ$$

Enthalpy [5.3]

CHEMICAL THERMODYNAMICS – deals with HEAT–WORK–OTHER ΔE in realtion fo chemical and physical phenomena



• positive q is heat flow in; negative q is heat flow out

• positive w if work is done on the system; and negative w if work is done by the system.

$$H = U + PV \quad \leftarrow arbitrary Def.$$
carit measure H directly, $\int bin can measure lifetime
$$\Delta H = \Delta U + P\Delta V + V\Delta P$$
@ constant pressure $\int \Delta P \rightarrow B \quad argon P = k$

$$\Delta H = \Delta U + P\Delta V$$

$$P\Delta V = -w \quad \qquad \Delta V \text{ and } w \text{ are opporte signs, by def.}$$

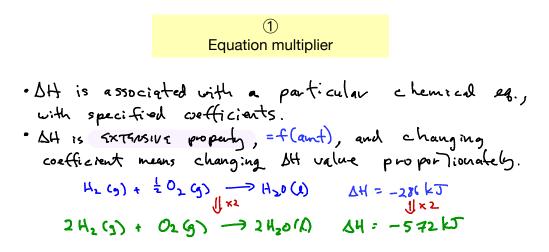
$$if \Delta V_{sys} = (+), then sys expands, \\then sys does look an sider, the $v = (-)$

$$\Delta H = \Delta U + P\Delta V \leftarrow expansion work$$

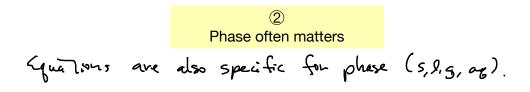
$$= (g_{P} + w) + (-w)$$
nead-to-line $\begin{cases} \Delta H = g_{P} \end{cases}$

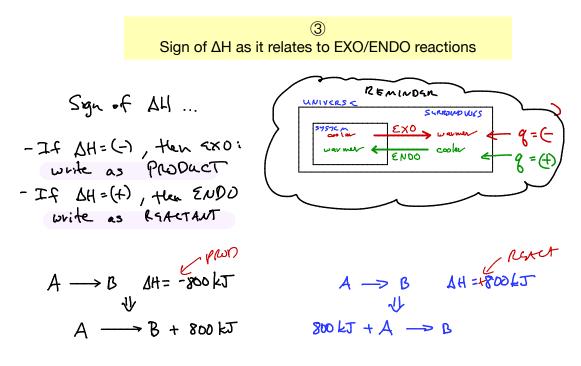
$$Euthelpy = Heat @ P = k \end{cases}$$$$$

Enthalpy as Reactant (or Product): Three useful conventions to remember









- Two types of problems
 - $\rightarrow \Delta H$ for rxn given, calc ΔH for given quantity of material
 - $\hookrightarrow \Delta H$ for quantity of material given, calc ΔH for rxn

Solutions (1) Amount of heat (ΔH) given for a specific quantity of reactant or product (2) Amount of heat (ΔH) given for a specific reaction equation Solutions (1) Amount of heat (ΔH) given for a specific quantity of reactant or product • Ratio an amount of reactant or product to the amount of heat generated/consumed • Use that ration as a CF, and use Dimensional Analysis to solve (2) Amount of heat (ΔH) given for a specific reaction equation • Use traditional stoichiometry to calculate the heat generated/consumed by a specific amount of reactant or product • The "box" belongs below the in-line heat value (i.e., in the mole hole"

(EX) Δ H for quantity of material given, calc Δ H(rxn) [ex 5.9] ;A gummy bear contains 2.67 g sucrose, C₁₁H₂₂O₁₁. When it reacts with 7.19 g potassium chlorate, KClO₃, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction, if sucrose is in excess...

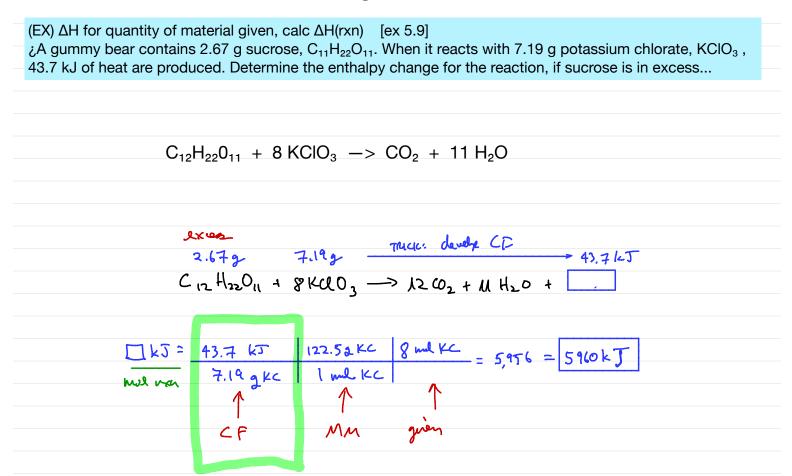
$C_{12}H_{22}O_{11} + 8 \text{ KCIO}_3 \rightarrow CO_2 + 11 \text{ H}_2O$

(1) Amount of heat (Δ H) given for a specific quantity of reactant or product

• Ratio an amount of reactant or product to the amount of heat generated/consumed

· Use that ration as a CF, and use Dimensional Analysis to solve





t

32.5 k = 2 21.6_{1} $CH_{3} \partial CH_{3} + \delta_{2} \rightarrow 2CO_{2} + 3H_{2} \partial + AH_{VCN}$

DKJ .	82.5 LJ	
mal usen		

DKJ.	82.5 2	46.02,12	1 ml ME	1450 KJ/ml vien	1454.02
mal usen	2.61 g, ME	1 molne	1 ml man -		

Standard State: The Reference Point for Thermodynamic Calculations

л.Ц°

Std Enthalpy of Combustion, ΔHc^{o}

 \rightarrow If ΔHc° given, then often becomes a probem of the type: 'ΔH for rxn given, calc ΔH for given quantity of material'

$$2 M + O_2 \rightarrow 2 MO$$

$$M_c^2 = -#$$

$$M_c^2 = -#$$

$$(4xo)$$
Examples
$$\frac{\text{Item}}{\text{carbon, c}} \qquad \frac{\Delta H^2_{\text{c}} (kT/\text{mod})}{-393.5}$$

$$M_g \qquad -60(.6)$$

$$CH_4 \qquad -890.8 \qquad \text{3vd hallest nature chan. flare}$$

$$HC \equiv CH \qquad -1,301.1 \qquad (360 \text{ K } /3330^{\circ}\text{C} / 600^{\circ}\text{F})$$

$$i - Cg \qquad -5441 \qquad \Rightarrow \text{flum Tage} (900^{\circ}\text{C} / 1650^{\circ}\text{F})$$

$$i + Cg \qquad -1366.8 \qquad \text{Text Book} \quad 4x.$$

Aside: Flane	Temp erctures :
Natur gas	2,070 %
Kero -	2,093

(EX) Δ H for quantity of material given, calc Δ H for rxn [ex 5.10b] ¿How much heat is produced by the combustion of 125 g of acetylene, given Δ Hc° = -1301.1 kJ/mol @ 25°C?

Standard Enthalpy of Formation

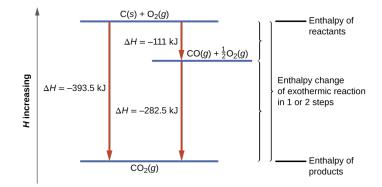
L> Essentially, the anount of heat it takes to produce 1 mole of compound firm "screatch" (elements), assuming the L> Stot Enthlogy of firmination of each element is zero (unless other wise noted). C(s) + O₂(g) → CO₂(g) All f = -393.5 kJ 1/2 N₂(g) + O₂(g) → NO₂(g) = +33.2 kJ (APPENDIX G)

(EX) Write Δ Hf Reaction [ex 5.12a] ¿Write the heat of reaction for C₂H₅OH, ethanol?

> Using APPENDIX G data: $2 C(s) + 3 H_2(g) + \frac{1}{2} 0_2(g) \rightarrow C_2 H_5 OH(\ell)$ All = -277.6 bt/ll $\int \int M_{res} dr dr$

Rack-n-stack two or more equations so the sum equals a Target (desired) equation.

$$\Delta H_{nxn} = \Delta H_{nxn} + \Delta H_{nxn} + \Delta H_{nxn} = \Sigma \Delta H_{nxn,i}$$



	AH 298
$(1) C_{(5)} + O_{2(j)} \rightarrow O_{1(j)}$	5) -394 kr
$ (2) (3) * \frac{1}{2}\partial_2(g) \rightarrow (0) g $) - I(I ⁻
$(3) \underbrace{co}_{(j)} + \frac{1}{2} \underbrace{c}_{(j)} \rightarrow \underbrace{co}_{(j)}$	5) -283
$(2+3-1) \zeta_{(5)} + 0_2 \zeta_{(5)} \longrightarrow (0_2 \zeta_{(5)})$) -394 k

(EX) HESS (2-tier+rev+multiplier) [ex 5.13b] ;Calc Δ H(rxn) for the equation: N₂ (g) + 2 O₂ (g) \rightarrow 2 NO₂ (g) given,

(a) $N_2(g) + O_2(g) \rightarrow 2 \text{ NO}(g) \longrightarrow + 80.5 \text{ kJ/hal non}$ +57.06 kJ/almen $NO_2(g) \rightarrow 2 NO(g) + \frac{1}{2} O_2(g)$ (b) N2 + 202 + 2NO2 Attpor = [TARGET + 180.5 N2 + 02 -> 2,00, + 1 2 N2 202 2102 4 +66.4KJ

Hess' Law and ΔHf° Combined

$$A + B \rightarrow C + D$$

$$\Delta H_{c}^{\circ}(\omega) \qquad \Delta H_{c}^{\circ}(\omega) \qquad \Delta H_{c}^{\circ}(\omega) \qquad \Delta H_{c}^{\circ}(\omega) \qquad \Delta H_{c}^{\circ}(\omega) = \left[\Delta H_{c}^{\circ}(\omega) + \Delta H_{c}^{\circ}(\omega)\right] - \left[\Delta H_{c}^{\circ}(\omega) - \Delta H_{c}^{\circ}(\omega)\right] - \left[\Delta H$$

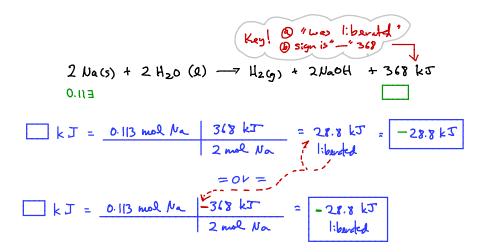
(EX) Hess: Calc ΔH° from Reactant & Prod ΔHf° values [5.15b] ¿Calc ΔH (comb) for 1 mole of ethanol, C₂H₅OH(ℓ), given ΔH° (form) value for C₂H₅OH(ℓ) (–278 kJ/mol), H₂O (-286), and CO₂ (-394)?

Question
reg.
1 (2H50H + 302
$$\rightarrow$$
 2C02+ 3H20 + 1368 for
1 (-278) 3(8) 2(394) 3(-286)
prod
AH_f = [MOD] - [RMCT] = [2(-394) + 3(-286] - [1(-278) + 3(8)]
= [-788 + -850] + [+278]
= [-1646] + [278]
AH_{vxn} = -1368 kJ/me rxn

Exam Review Practice Problems

(EX) Calculate Δ H(liberated) based on Δ H(std rxn)

¿How much heat is liberated when 0.113 mole of sodium reacts with excess water, according to the equation what has a Δ H(rxn) value of –368 kJ/mol rxn?



- CAVEAT !!! A word problem may not state the vale is exothermic, nother, a physice such as "liberates" or "is given off" may be used.
- If one says "I broad " or "I gave " you \$20, you are responsible to know whether you need to debit their accord (- \$20), or credit their act. (+\$20)

(EX) Calculate exotherm from ΔH data

How much heat is given off when 24.2 g of Al is oxidized to aluminum oxide at 25 °Ca nd 1 atm? ($\Delta H^{\circ} = -3352 \text{ kJ/mol rxn}$)

$$24.29
4AR + 30_2 \rightarrow 2AR_20_7 + 3352 kJ$$

$$kJ = 24.29AL | mol AL | mol van | -3352 kJ = 752 kJ$$

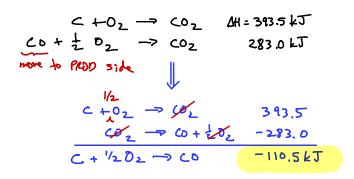
$$26.815 AL | 4 mol kL | mol van | = 752 kJ$$

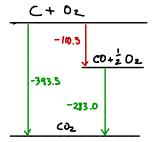
(EX) Calculate ΔH° (formation) data ¿Given the following equation, determine ΔH° f for HBr?

$$H_{2} + Bv_{2} \rightarrow 2HBr_{2} \qquad \Delta H^{\circ} = -78.2 \text{ kJ/hol ven}$$

by definition of "formation"
why need 1 mol Br_{2} = 2

$$\frac{1}{2}H_{2} + \frac{1}{2}Bv_{2} \rightarrow HBr \qquad \Delta H^{\circ} = \frac{1}{2}(-78.2) = -36.4 \text{ kJ/hol Her}$$





EX: HESS (3 tier + rever	se + multiplier)
¿ Calc AH for: C+H2→	CH4, given:
$ \begin{array}{c} c + 0_2 \longrightarrow c 0_2 \end{array} $	AH (H20's must cancel out must be on opposite
	- 393.5) sides, AND
(b) $H_1 + \frac{1}{2} \partial_2 \longrightarrow H_2 0 \swarrow$	-235.8 ×2 . must have same Coeff.
	- 890.3 <u>en reverse</u> vxn (c)
PROPRIET U	
C+ & -> COZ	~ 393.5
$2H_{L} + d_{2} \rightarrow 2H_{20}$	2 (-285.8)
(+2+2+20 → CH4+2Q.	+ 890.3
C+2H2 -> CH4	-74.8 kJ

$$C_{2}H_{4} + H_{2}\partial(R) \rightarrow C_{2}H_{5}OH(R)$$
need to be $\frac{3iven!}{c_{2}H_{4} + 30_{2}} \rightarrow 2c\partial_{2} + 3H_{2}\partial - 13(7)$

$$C_{2}H_{4} + 30_{2} \rightarrow 2c\partial_{2} + 2H_{2}O - 1411$$
hasds to be $\frac{1}{c_{2}H_{4} + 30_{2}} \rightarrow 2c\partial_{2} + 2H_{2}O - 1411$

$$\frac{2c\partial_{2} + \frac{1}{2}H_{2}O}{c_{2}H_{4} + 30_{2}} \rightarrow 2c\partial_{2} + 2H_{2}O - 1411$$

$$\frac{2c\partial_{2} + \frac{1}{2}H_{2}O}{c_{2}H_{4} + 30_{2}} \rightarrow 2c\partial_{2} + 2H_{2}O - 1411$$

$$\frac{1367}{c_{2}H_{4} + 4_{2}O(R)} \rightarrow c_{2}H_{5}OH(R) + 3d_{2} - 1411$$

$$\frac{1367}{c_{2}H_{4} + 4_{2}O(R)} \rightarrow c_{2}H_{5}OH(R) - 44 \frac{13}{4}$$

EX: Cale Alfren from Attennation Data

i Calc Attven for the following vxn, wing Att values from a dota table? Altr (c2H50H) = -277.7 Kml; (c2H4) =

 $C_2H_4 + H_2O(2) \longrightarrow C_2H_3OH$ $AH_f + 52.3 - 285.8 - 277,7$

$$\Delta 4_{KKN} = [-277,7] - [(52,3) + (285.8)]$$

$$A 4_{KKN} = [-277,7] - [-233.5]$$

$$A 4_{KKN} = -44.2 \text{ ks/mol}$$

