

[TP] The enthalpy diagram shows changes associated with the reaction

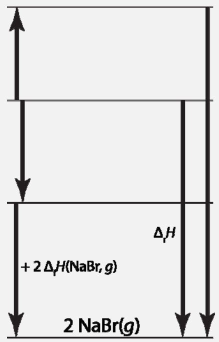
$Na_2(g) + Br_2(g) \rightarrow 2\ NaBr(g)$.

The small upward arrow is the enthalpy change, ΔH, of

$Na_2(g) + Br_2(g) \rightarrow 2\ Na(g) + 2\ Br(g)$.

The corresponding energy change, ΔU, is …

25% 1. larger than ΔH
25% 2. equal to ΔH
25% 3. smaller than ΔH
25% 4. Further information needed



Lecture 26 CH101 A2 (MWF 11:15 am)

Wednesday, November 7, 2018

For today …

- Using $\Delta_f H°$ to compute *any* $\Delta_r H$;
- Bond enthalpies, $\Delta_b H$
- Using $\Delta_b H$ to *estimate* $\Delta_r H$;
- If some substances are not gases, using $\Delta_b H$ works poorly

Next lecture: Begin ch 8: Modeling atoms and their electrons: Review: What light is and how it interacts with matter ; Natural frequencies of atoms ; Light and matter exchange energy smoothly and slowly

Prepare: Hydrogen atom family album, https://goo.gl/XPkcxv

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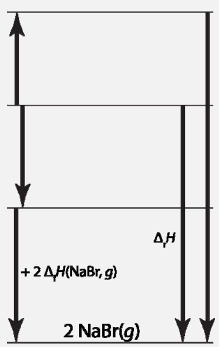

Using $\Delta_f H°$'s to compute $\Delta_r H$

$$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

Using $\Delta_f H°$'s to compute $\Delta_r H$

$$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

$4\ NH_3(g) \rightarrow 2\ N_2(g) + 6\ H_2(g)$ $\quad \Delta H_1 = -\ 4\ \Delta H_f(NH_3, g)$

$5\ O_2(g) \rightarrow 5\ O_2(g)$ $\quad \Delta H_2 = 0$

$2\ O_2(g) + 2\ N_2(g) \rightarrow 4\ NO(g)$ $\quad \Delta H_3 = +\ 4\ \Delta H_f(NO, g)$

$6\ H_2(g) + 3\ O_2(g) \rightarrow 6\ H_2O(g)$ $\quad \Delta H_4 = +\ 6\ \Delta H_f(H_2O, g)$

Hess's law: $\Delta_r H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

$= +\ 4\ \Delta H_f(NO, g) + 6\ \Delta H_f(H_2O, g) - 4\ \Delta H_f(NH_3, g)$

Note: Elements in standard states are absent

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Using $\Delta_f H°$'s to compute any $\Delta_r H$

The key feature of standard enthalpies of formation is that, the enthalpy change of any reaction, $\Delta_r H$, can be computed using them, as …

$$\Delta_r H = \text{Sum}[\Delta_f H(\text{products})] - \text{Sum}[\Delta_f H(\text{reactants})]$$

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Using $\Delta_b H$'s to *estimate* $\Delta_r H$

$AB(g) \rightarrow A(g) + B(g) \quad \Delta H \equiv \Delta_b H$

TABLE 7.3
Average Values of Some Single- and Multiple-Bond Energies (kJ mol^{-1})

Source: I. Klotz and R.M. Rosenberg, *Chemical Thermodynamics*, 4th ed., p. 55, New York: John Wiley, 1994; and J.E. Huheey, E.A. Keiter, and R.L. Keiter, *Inorganic Chemistry*, 4th ed., Table E.1, New York: HarperCollins, 1993.

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	413	391	463	565	328	322	347	432	366	299
C		346	305	358	485	–	–	272	339	285	213
N			163	201	283	–	–	–	192	–	–
O				146	–	452	335	–	218	201	201
F					155	565	490	284	253	249	278
Si						222	–	293	381	310	234
P							201	–	326	–	184
S								226	255	–	–
Cl									242	216	208
Br										193	175
I											151

Multiple Bonds

N=N	418	C=C	610
N≡N	945	C≡C	835
C=N	615	C=O	745
C≡N	887	C≡O	1046
O=O (in O_2)	498		

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Using $\Delta_b H$'s to *estimate* $\Delta_r H$

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

How much enthalpy change to break reactants apart into atoms?

$2\ H_2(g) \rightarrow 4\ H(g) \quad \Delta H = 2 \times 436$ kJ

$O_2(g) \rightarrow 2\ O(g) \quad \Delta H = 498$ kJ

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How much enthalpy change to combine reactant atoms into products?

$4\ H(g) + 2\ O(g) \rightarrow 2\ H_2O(g) \qquad \Delta H = -(4 \times 463)\ kJ$

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Using $\Delta_b H$'s to *estimate* $\Delta_r H$

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

How much enthalpy change to break reactants apart into atoms?

$2\ H_2(g) \rightarrow 4\ H(g) \qquad \Delta H_1 = 2 \times 436\ kJ$

$O_2(g) \rightarrow 2\ O(g) \qquad \Delta H_2 = 498\ kJ$

How much enthalpy change to combine reactant atoms into products?

$4\ H(g) + 2\ O(g) \rightarrow 2\ H_2O(g) \qquad \Delta H_3 = -(4 \times 463)\ kJ$

What is the estimated total enthalpy change?

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -482\ kJ$

The exact value is

$2 \times \Delta_f H(H_2O, g) = -483.66\ kJ$

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Using $\Delta_b H$'s to *estimate* $\Delta_r H$

The key feature of standard bond dissociation energies is that, the enthalpy change of any reaction, $\Delta_r H$, can be estimated using them, as …

$\Delta_r H$ = Sum[energy spent breaking bonds] –

Sum[energy evolved forming bonds]

= Sum[$\Delta_b H$(reactants)] – Sum[$\Delta_b H$(products)]

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[Quiz] "In my lecture I was told that change in enthalpy is products minus reactants, but my discussion leader told me that it is reactants minus products. I've also looked in another chemistry book and it say products minus reactants. Which is right?"

25% 1. products minus reactants
25% 2. reactants minus products
25% 3. both
25% 4. neither

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If some substances are not gases, using $\Delta_b H$ works poorly

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$\Delta_f H°$ versus $\Delta_b H$ to compute $\Delta_r H$

$$C_2H_5OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

Using standard enthalpies of formation:

$$\Delta_r H = +\ 2\ \Delta H_f(CO_2, g) + 3\ \Delta H_f(H_2O, g) - \Delta H_f(C_2H_5OH, g) = -\ 1{,}277.38\ \text{kJ}$$

Using bond enthalpies:

$$\Delta_r H = +\ \Delta H_{break}(C_2H_5OH) + 3\ \Delta H_{break}(O_2) - 2\ \Delta H_{make}(CO_2) - 3\ \Delta H_{make}(H_2O) = -\ 1{,}232\ \text{kJ}$$

Good agreement!

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$\Delta_f H°$ versus $\Delta_b H$ to compute $\Delta_r H$

$$C(s, gr) + 2\ H_2O(g) \rightarrow CH_4(g) + O_2(g)$$

Using standard enthalpies of formation:

$$\Delta_r H = +\ \Delta H_f(CH_4, g) -\ 2\ \Delta H_f(H_2O, g)$$
$$= -\ 74.81 - 2(-\ 241.82) = +\ 408.83\ \text{kJ}\ (actual)$$

Using bond enthalpies:

$$\Delta_r H = +\ 2\ \Delta H_{break}(H_2O) - \Delta H_{make}(CH_4) - \Delta H_{make}(O_2)$$
$$= +\ 4\ (\text{O-H}) - 4(\text{C-H}) - (\text{O=O})$$
$$= 4(460) - 4(414) - 498.7 = -\ 315\ \text{kJ}\ (approximate)$$

Big error!

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$\Delta_f H°$'s versus $\Delta_b H$'s to compute $\Delta_r H$

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$$= -\ 74.81 - 2(-\ 241.82) = +\ 408.83\ \text{kJ}\ (actual)$$

Using bond enthalpies:

$$C(s, gr) \rightarrow C(g),\ \Delta H_f(C, g) = 716.7\ \text{kJ}$$
$$C(g) + 2\ H_2O(g) \rightarrow CH_4(g) + O_2(g),\ -\ 315\ \text{kJ}\ (approximate)$$
$$\Delta_r H = 716.7\ \text{kJ} - 315\ \text{kJ} = +\ 402\ \text{kJ}\ (approximate)$$

Much better!

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