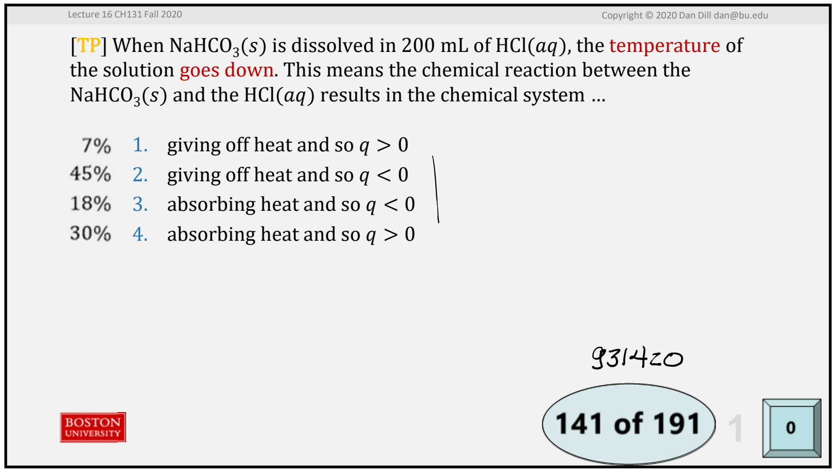

[TP] When $NaHCO_3(s)$ is dissolved in 200 mL of $HCl(aq)$, the temperature of the solution goes down. This means the chemical reaction between the $NaHCO_3(s)$ and the $HCl(aq)$ results in the chemical system …

7%	1.	giving off heat and so $q > 0$
45%	2.	giving off heat and so $q < 0$
18%	3.	absorbing heat and so $q < 0$
30%	4.	absorbing heat and so $q > 0$

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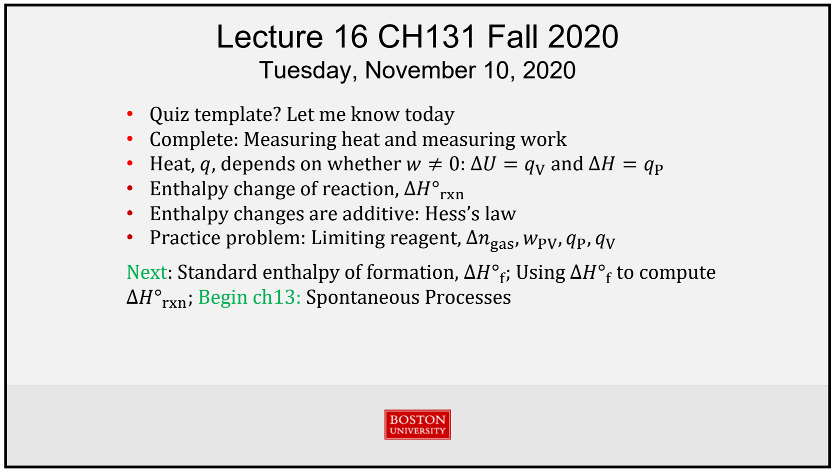
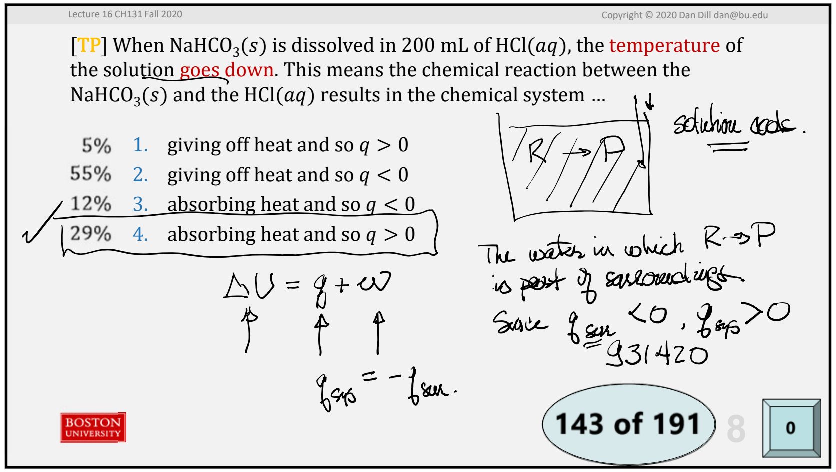


Lecture 16 CH131 Fall 2020

Tuesday, November 10, 2020

- Quiz template? Let me know today
- Complete: Measuring heat and measuring work
- Heat, q, depends on whether $w \neq 0$: $\Delta U = q_V$ and $\Delta H = q_P$
- Enthalpy change of reaction, $\Delta H°_{rxn}$
- Enthalpy changes are additive: Hess's law
- Practice problem: Limiting reagent, Δn_{gas}, w_{PV}, q_P, q_V

Next: Standard enthalpy of formation, $\Delta H°_f$; Using $\Delta H°_f$ to compute $\Delta H°_{rxn}$; Begin ch13: Spontaneous Processes



[TP] When $NaHCO_3(s)$ is dissolved in 200 mL of $HCl(aq)$, the temperature of the solution goes down. This means the chemical reaction between the $NaHCO_3(s)$ and the $HCl(aq)$ results in the chemical system …

5%	1.	giving off heat and so $q > 0$
55%	2.	giving off heat and so $q < 0$
12%	3.	absorbing heat and so $q < 0$
✓ 29%	4.	absorbing heat and so $q > 0$

$R \to P$

solution cools.

The water in which $R \to P$ is part of surroundings.

Since $q_{surr} < 0$, $q_{sys} > 0$

$\Delta U = q + w$

$q_{sys} = -q_{surr}$.

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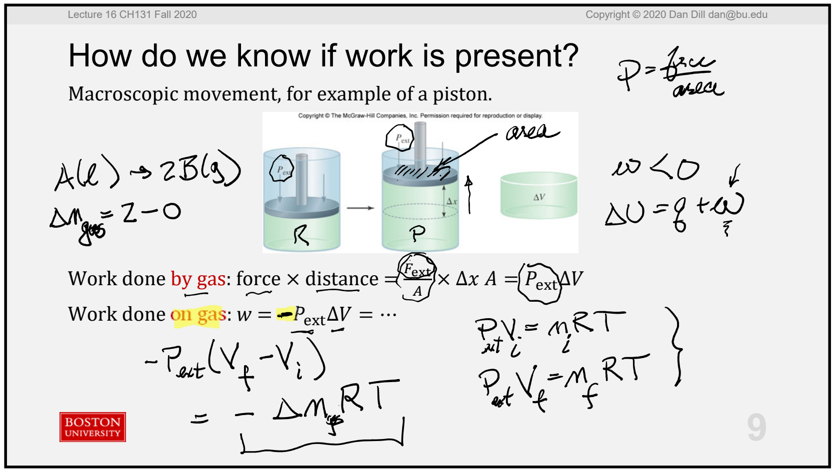

How do we know if work is present?

$P = \frac{\text{force}}{\text{area}}$

Macroscopic movement, for example of a piston.

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$A(l) \to 2B(g)$

$\Delta n_{gas} = 2 - 0$

$w < 0$

$\Delta U = q + w$

Work done by gas: force × distance $= \frac{F_{ext}}{A} \times \Delta x\, A = P_{ext} \Delta V$

Work done on gas: $w = -P_{ext} \Delta V = \cdots$

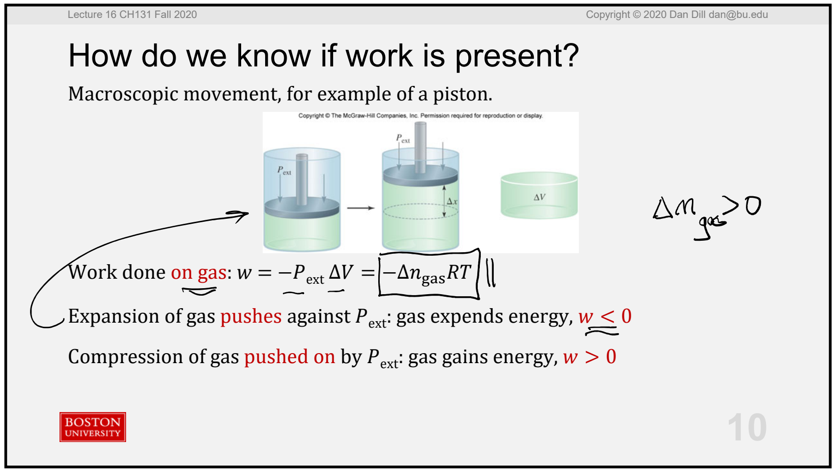
$-P_{ext}(V_f - V_i)$

$= -\Delta n_g RT$

$P_{ext} V_i = n_i RT$

$P_{ext} V_f = n_f RT$

9



How do we know if work is present?

Macroscopic movement, for example of a piston.

$\Delta n_{gas} > 0$

Work done on gas: $w = -P_{ext}\,\Delta V = \boxed{-\Delta n_{gas}RT}$ ||

Expansion of gas pushes against P_{ext}: gas expends energy, $w \le 0$

Compression of gas pushed on by P_{ext}: gas gains energy, $w > 0$

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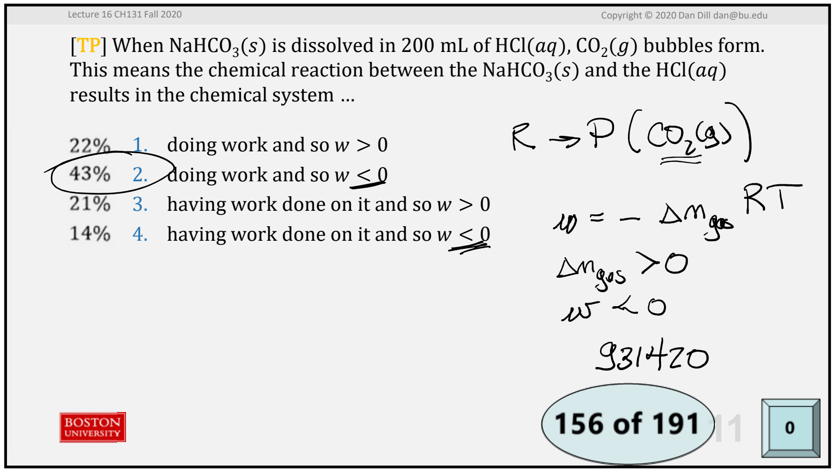

[TP] When $NaHCO_3(s)$ is dissolved in 200 mL of $HCl(aq)$, $CO_2(g)$ bubbles form. This means the chemical reaction between the $NaHCO_3(s)$ and the $HCl(aq)$ results in the chemical system …

22% 1. doing work and so $w > 0$
[✓ 43% 2. doing work and so $w \le 0$]
21% 3. having work done on it and so $w > 0$
14% 4. having work done on it and so $w \le 0$

$R \rightarrow P\,(CO_2(g))$

$w = -\Delta n_{gas} RT$

$\Delta n_{gas} > 0$

$w < 0$

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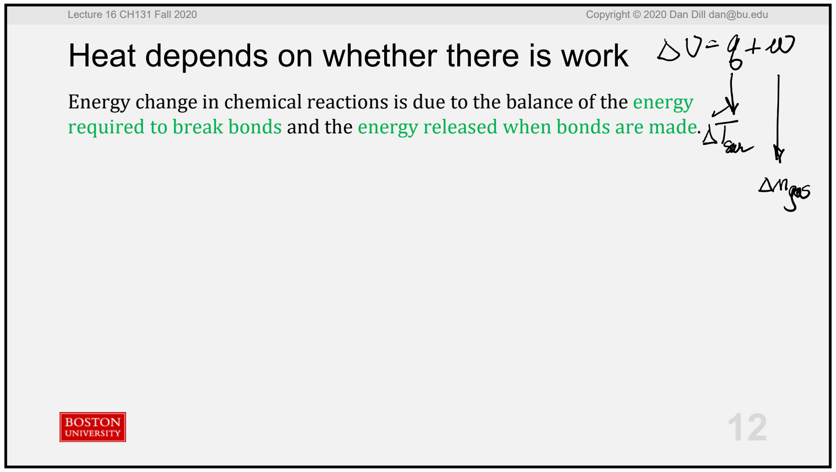

Heat depends on whether there is work

$\Delta U = q + w$

Energy change in chemical reactions is due to the balance of the energy required to break bonds and the energy released when bonds are made.

ΔT_{sur}

Δn_{gas}

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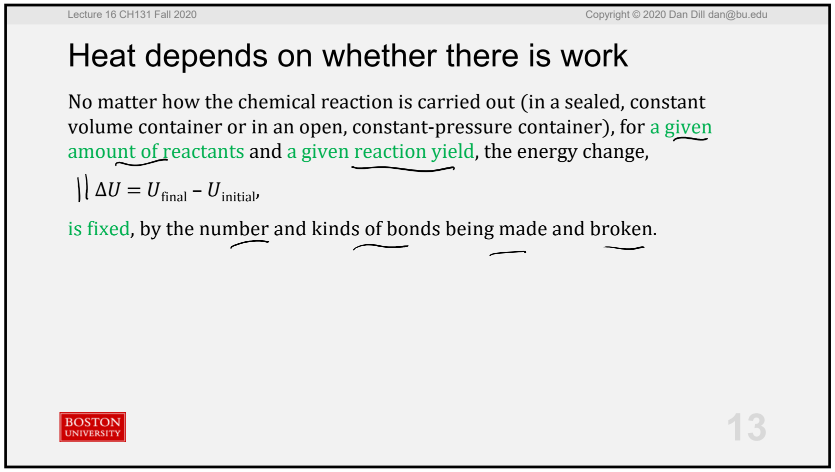

Heat depends on whether there is work

No matter how the chemical reaction is carried out (in a sealed, constant volume container or in an open, constant-pressure container), for a given amount of reactants and a given reaction yield, the energy change,

|| $\Delta U = U_{final} - U_{initial}$,

is fixed, by the number and kinds of bonds being made and broken.

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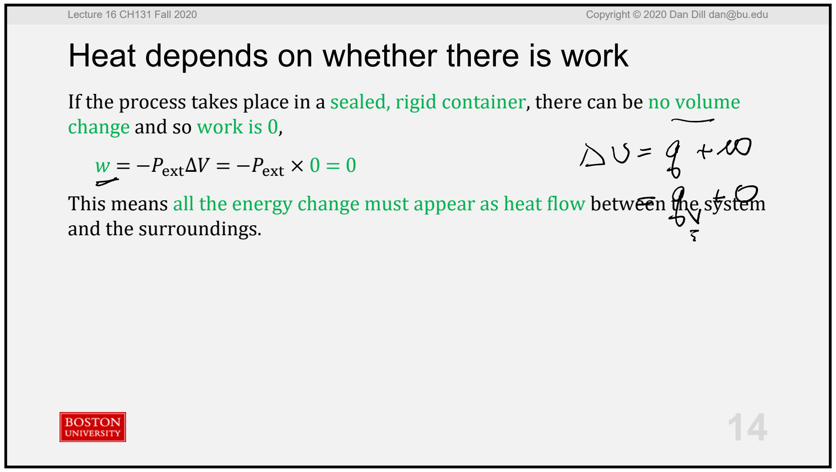

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Heat depends on whether there is work

If the process takes place in a sealed, rigid container, there can be no volume change and so work is 0,

$$w = -P_{\text{ext}}\Delta V = -P_{\text{ext}} \times 0 = 0$$

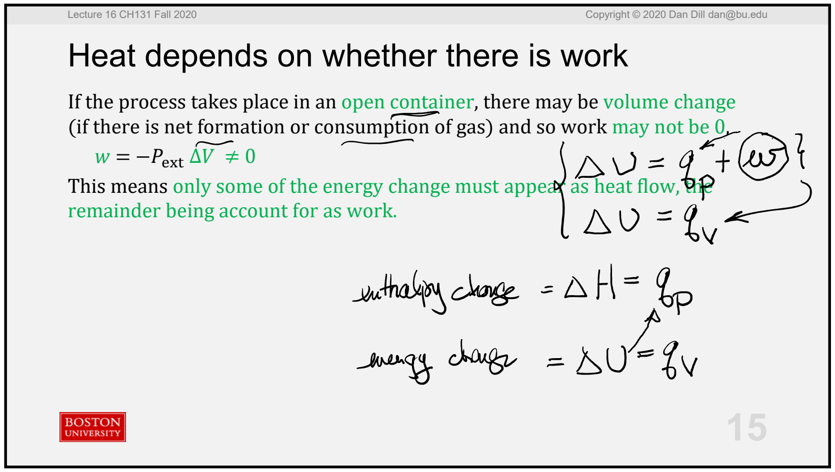
This means all the energy change must appear as heat flow between the system and the surroundings.

$\Delta U = q + w$

$= q_V + 0$

14

14



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Heat depends on whether there is work

If the process takes place in an open container, there may be volume change (if there is net formation or consumption of gas) and so work may not be 0,

$$w = -P_{\text{ext}}\,\Delta V \neq 0$$

This means only some of the energy change must appear as heat flow, the remainder being account for as work.

$\Delta U = q_P + w$

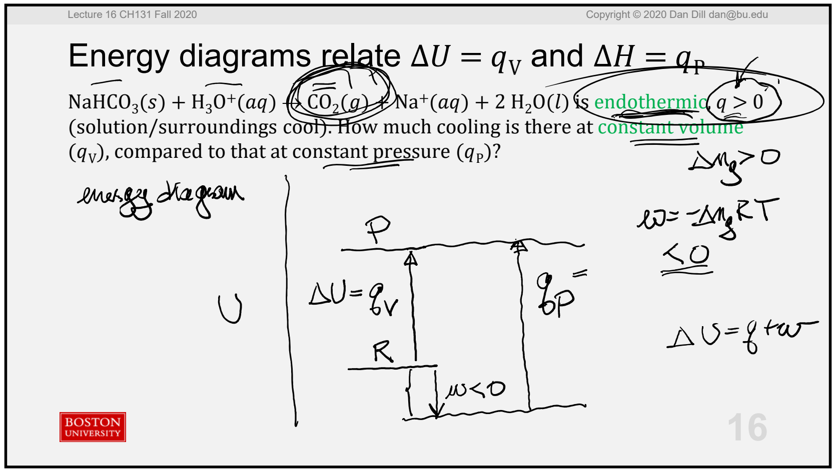
$\Delta U = q_V$

enthalpy change $= \Delta H = q_P$

energy change $= \Delta U = q_V$

15

15



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Energy diagrams relate $\Delta U = q_V$ and $\Delta H = q_P$

$NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, $q > 0$ (solution/surroundings cool). How much cooling is there at constant volume (q_V), compared to that at constant pressure (q_P)?

energy diagram

$\Delta n_g > 0$

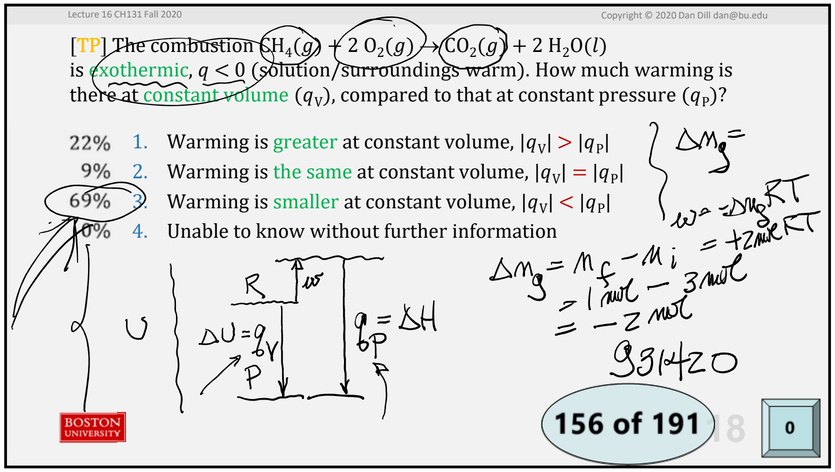
$w = -\Delta n_g RT$

< 0

$\Delta U = q + w$

16

16



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[TP] The combustion $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ is exothermic, $q < 0$ (solution/surroundings warm). How much warming is there at constant volume (q_V), compared to that at constant pressure (q_P)?

22%	1.	Warming is greater at constant volume, $\lvert q_V \rvert > \lvert q_P \rvert$
9%	2.	Warming is the same at constant volume, $\lvert q_V \rvert = \lvert q_P \rvert$
69%	3.	Warming is smaller at constant volume, $\lvert q_V \rvert < \lvert q_P \rvert$
0%	4.	Unable to know without further information

$\Delta n_g =$

$w = -\Delta n_g RT$

$= +2\text{ mol } RT$

$\Delta n_g = n_f - n_i$

$= 1\text{ mol} - 3\text{ mol}$

$= -2\text{ mol}$

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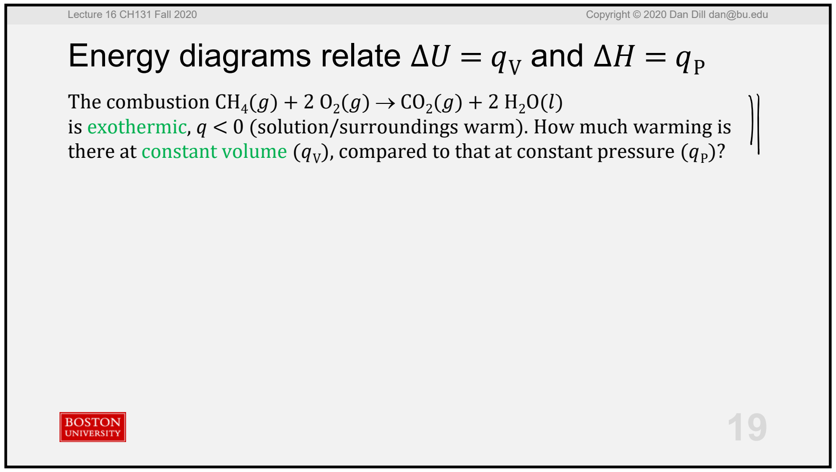

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Energy diagrams relate $\Delta U = q_V$ and $\Delta H = q_P$

The combustion $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ is exothermic, $q < 0$ (solution/surroundings warm). How much warming is there at constant volume (q_V), compared to that at constant pressure (q_P)?

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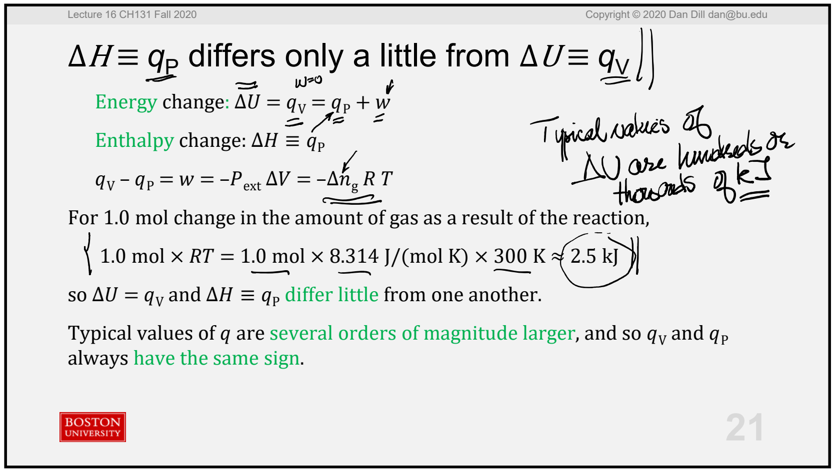

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$\Delta H \equiv q_P$ differs only a little from $\Delta U \equiv q_V$

Energy change: $\Delta U = \overset{w=0}{q_V} = q_P + w$

Enthalpy change: $\Delta H \equiv q_P$

$q_V - q_P = w = -P_{ext}\,\Delta V = \underline{-\Delta n_g\, R\, T}$

Typical values of ΔU are hundreds or thousands of kJ

For 1.0 mol change in the amount of gas as a result of the reaction,

$$1.0\text{ mol} \times RT = 1.0\text{ mol} \times 8.314\text{ J/(mol K)} \times 300\text{ K} \approx 2.5\text{ kJ}$$

so $\Delta U = q_V$ and $\Delta H \equiv q_P$ differ little from one another.

Typical values of q are several orders of magnitude larger, and so q_V and q_P always have the same sign.

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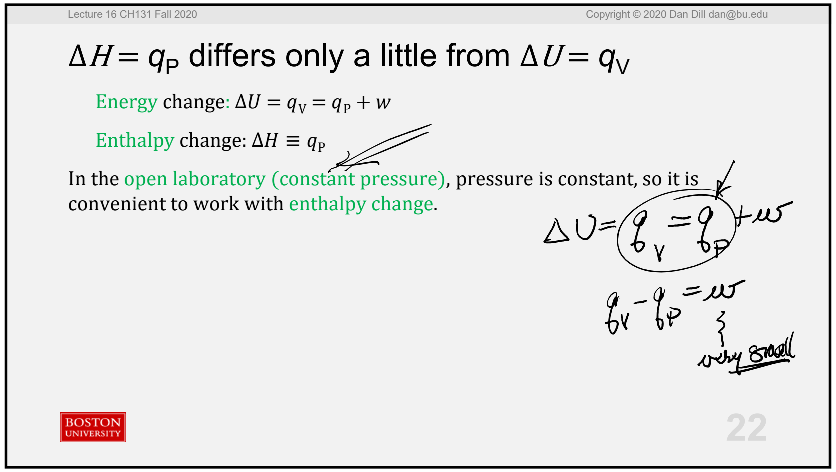

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$\Delta H = q_P$ differs only a little from $\Delta U = q_V$

Energy change: $\Delta U = q_V = q_P + w$

Enthalpy change: $\Delta H \equiv q_P$

In the open laboratory (constant pressure), pressure is constant, so it is convenient to work with enthalpy change.

$$\Delta U = q_V = q_P + w$$

$$q_V - q_P = \underbrace{w}_{\text{very small}}$$

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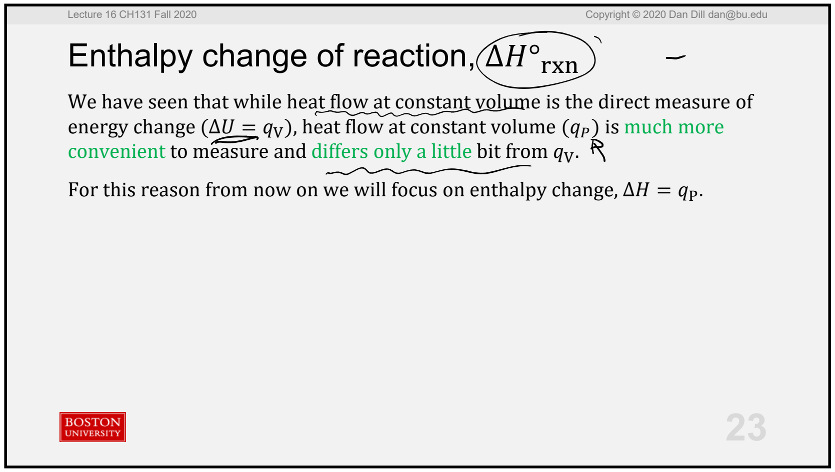

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Enthalpy change of reaction, $\Delta H°_{rxn}$

We have seen that while heat flow at constant volume is the direct measure of energy change ($\Delta U = q_V$), heat flow at constant volume (q_P) is much more convenient to measure and differs only a little bit from q_V.

For this reason from now on we will focus on enthalpy change, $\Delta H = q_P$.

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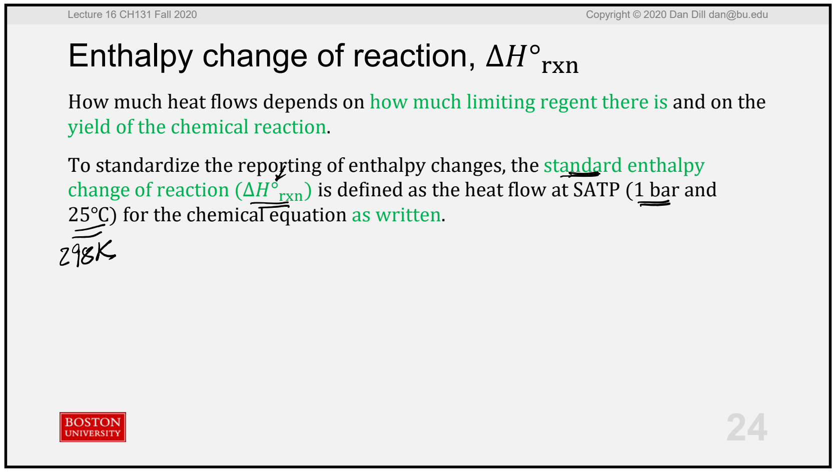

Enthalpy change of reaction, $\Delta H°_{\mathrm{rxn}}$

How much heat flows depends on how much limiting regent there is and on the yield of the chemical reaction.

To standardize the reporting of enthalpy changes, the standard enthalpy change of reaction ($\Delta H°_{\mathrm{rxn}}$) is defined as the heat flow at SATP (1 bar and 25℃) for the chemical equation as written.

298K

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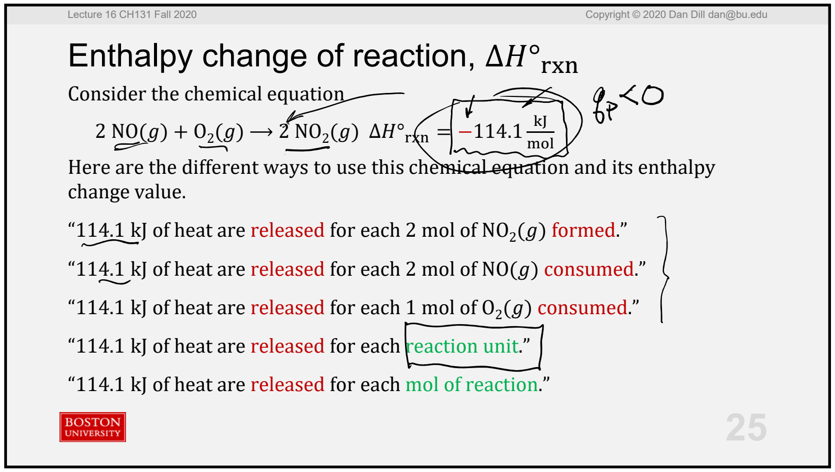

Enthalpy change of reaction, $\Delta H°_{\mathrm{rxn}}$

Consider the chemical equation

$$2\ \mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g)\quad \Delta H°_{\mathrm{rxn}} = \boxed{-114.1\ \frac{\mathrm{kJ}}{\mathrm{mol}}}$$

$q_P < 0$

Here are the different ways to use this chemical equation and its enthalpy change value.

"114.1 kJ of heat are released for each 2 mol of $NO_2(g)$ formed."

"114.1 kJ of heat are released for each 2 mol of $NO(g)$ consumed."

"114.1 kJ of heat are released for each 1 mol of $O_2(g)$ consumed."

"114.1 kJ of heat are released for each reaction unit."

"114.1 kJ of heat are released for each mol of reaction."

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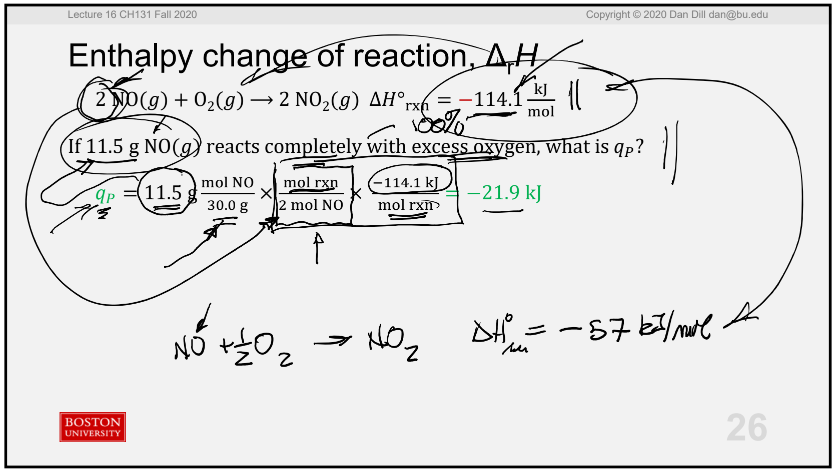

Enthalpy change of reaction, $\Delta_r H$

$$2\ \mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g)\quad \Delta H°_{\mathrm{rxn}} = -114.1\ \frac{\mathrm{kJ}}{\mathrm{mol}}$$

100%

If 11.5 g NO(g) reacts completely with excess oxygen, what is q_P?

$$q_P = 11.5\ \mathrm{g}\ \frac{\mathrm{mol\ NO}}{30.0\ \mathrm{g}} \times \boxed{\frac{\mathrm{mol\ rxn}}{2\ \mathrm{mol\ NO}} \times \frac{-114.1\ \mathrm{kJ}}{\mathrm{mol\ rxn}}} = -21.9\ \mathrm{kJ}$$

$$\mathrm{NO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NO_2} \qquad \Delta H°_{\mathrm{rxn}} = -57\ \mathrm{kJ/mol}$$

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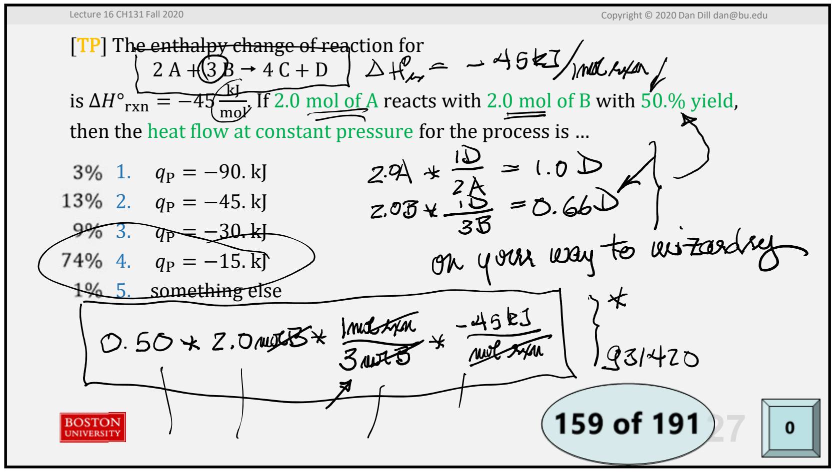

[TP] The enthalpy change of reaction for

$$\boxed{2\ \mathrm{A} + 3\ \mathrm{B} \rightarrow 4\ \mathrm{C} + \mathrm{D}} \qquad \Delta H°_{\mathrm{rxn}} = -45\ \mathrm{kJ/mol\ rxn}$$

is $\Delta H°_{\mathrm{rxn}} = -45\ \frac{\mathrm{kJ}}{\mathrm{mol}}$. If 2.0 mol of A reacts with 2.0 mol of B with 50.% yield, then the heat flow at constant pressure for the process is …

3% 1. $q_P = -90.\ \mathrm{kJ}$

13% 2. $q_P = -45.\ \mathrm{kJ}$

9% 3. $q_P = -30.\ \mathrm{kJ}$

74% 4. $q_P = -15.\ \mathrm{kJ}$

1% 5. something else

$$2.0\mathrm{A} * \frac{1\mathrm{D}}{2\mathrm{A}} = 1.0\ \mathrm{D}$$

$$2.0\mathrm{B} * \frac{1\mathrm{D}}{3\mathrm{B}} = 0.66\mathrm{D}$$

on your way to wizardry

$$\boxed{0.50 * 2.0\ \cancel{\mathrm{mol\ B}} * \frac{1\ \mathrm{mol\ rxn}}{3\ \cancel{\mathrm{mol\ B}}} * \frac{-45\ \mathrm{kJ}}{\cancel{\mathrm{mol\ rxn}}}}$$

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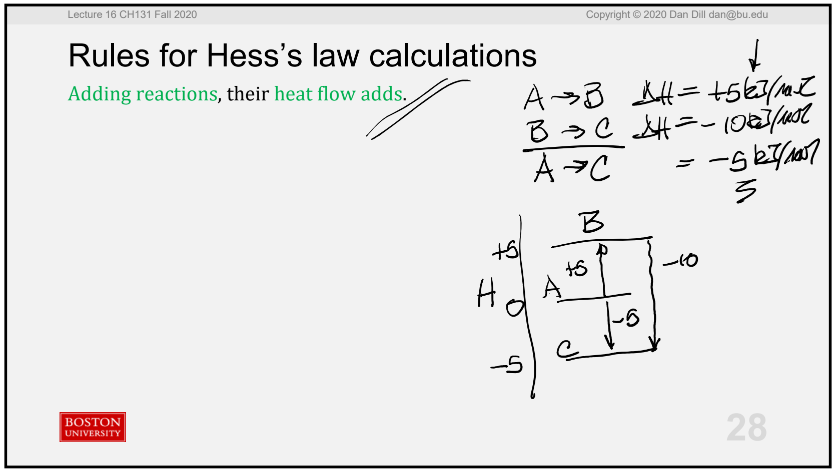

Rules for Hess's law calculations

Adding reactions, their heat flow adds.

$A \rightarrow B \quad \Delta H = +5\ \mathrm{kJ/mol}$

$B \rightarrow C \quad \Delta H = -10\ \mathrm{kJ/mol}$

$A \rightarrow C \quad = -5\ \mathrm{kJ/mol}$

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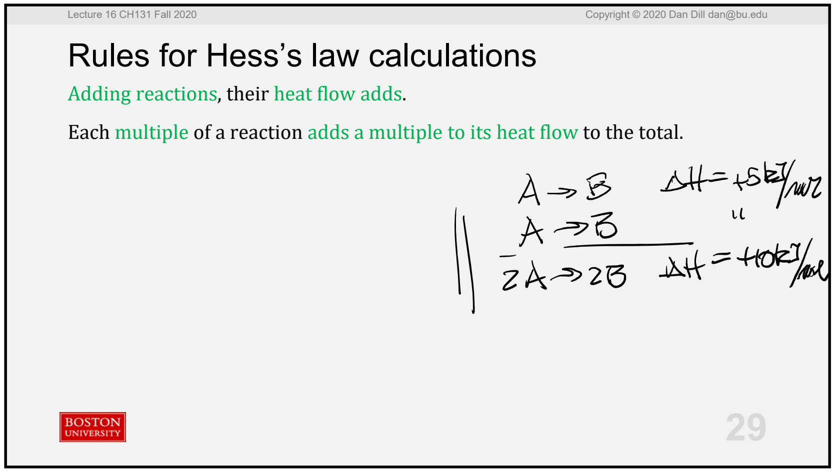

Rules for Hess's law calculations

Adding reactions, their heat flow adds.

Each multiple of a reaction adds a multiple to its heat flow to the total.

$A \rightarrow B \quad \Delta H = +5\ \mathrm{kJ/mol}$

$A \rightarrow B \quad ''$

$2A \rightarrow 2B \quad \Delta H = +10\ \mathrm{kJ/mol}$

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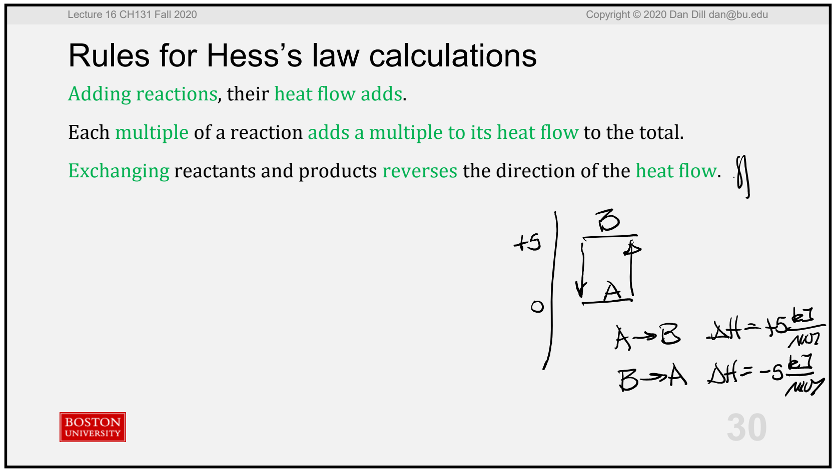


Rules for Hess's law calculations

Adding reactions, their heat flow adds.

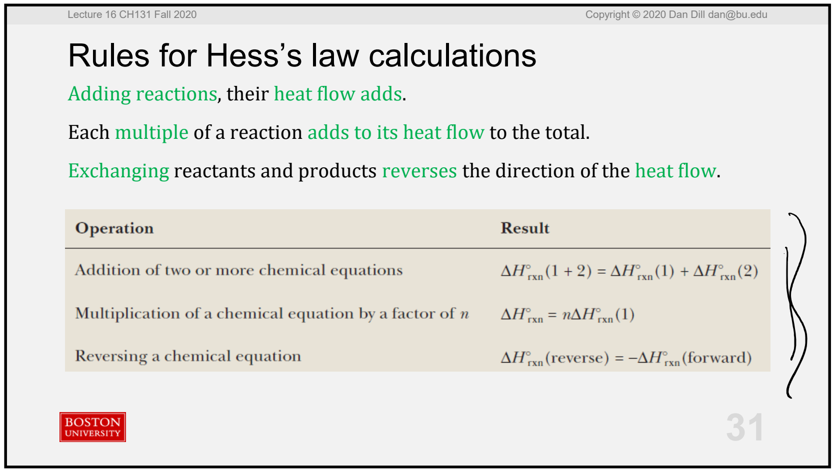
Each multiple of a reaction adds a multiple to its heat flow to the total.

Exchanging reactants and products reverses the direction of the heat flow.

$A \rightarrow B \quad \Delta H = +5\ \frac{\mathrm{kJ}}{\mathrm{mol}}$

$B \rightarrow A \quad \Delta H = -5\ \frac{\mathrm{kJ}}{\mathrm{mol}}$

30



Rules for Hess's law calculations

Adding reactions, their heat flow adds.

Each multiple of a reaction adds to its heat flow to the total.

Exchanging reactants and products reverses the direction of the heat flow.

Operation	Result
Addition of two or more chemical equations	$\Delta H^\circ_{\mathrm{rxn}}(1+2) = \Delta H^\circ_{\mathrm{rxn}}(1) + \Delta H^\circ_{\mathrm{rxn}}(2)$
Multiplication of a chemical equation by a factor of n	$\Delta H^\circ_{\mathrm{rxn}} = n\Delta H^\circ_{\mathrm{rxn}}(1)$
Reversing a chemical equation	$\Delta H^\circ_{\mathrm{rxn}}(\mathrm{reverse}) = -\Delta H^\circ_{\mathrm{rxn}}(\mathrm{forward})$

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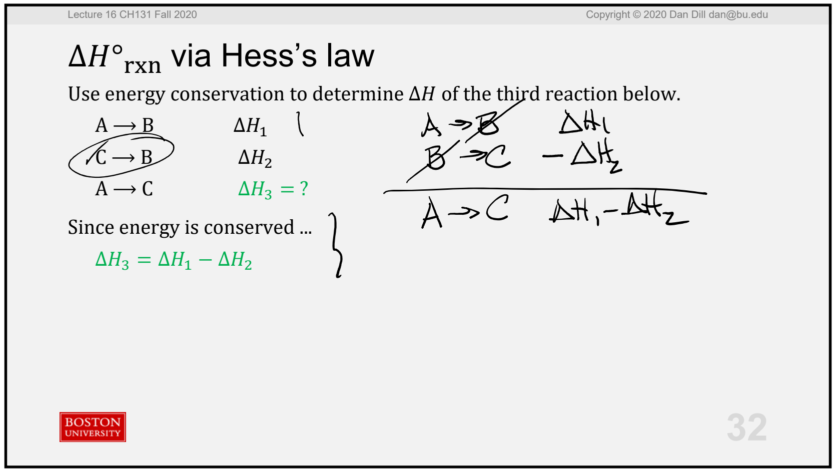


$\Delta H°_{\text{rxn}}$ via Hess's law

Use energy conservation to determine ΔH of the third reaction below.

$A \longrightarrow B$ ΔH_1

$C \longrightarrow B$ ΔH_2

$A \longrightarrow C$ $\Delta H_3 = ?$

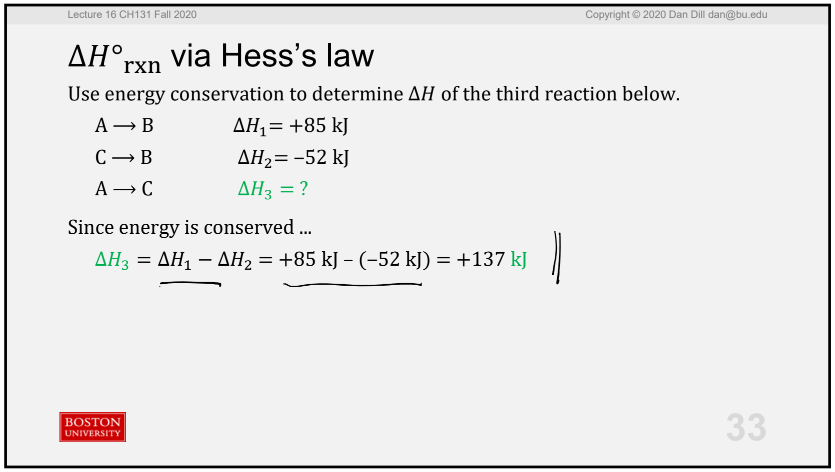
Since energy is conserved ...

$\Delta H_3 = \Delta H_1 - \Delta H_2$

$A \rightarrow \cancel{B}$ ΔH_1

$\cancel{B} \rightarrow C$ $-\Delta H_2$

$A \rightarrow C$ $\Delta H_1 - \Delta H_2$



$\Delta H°_{\text{rxn}}$ via Hess's law

Use energy conservation to determine ΔH of the third reaction below.

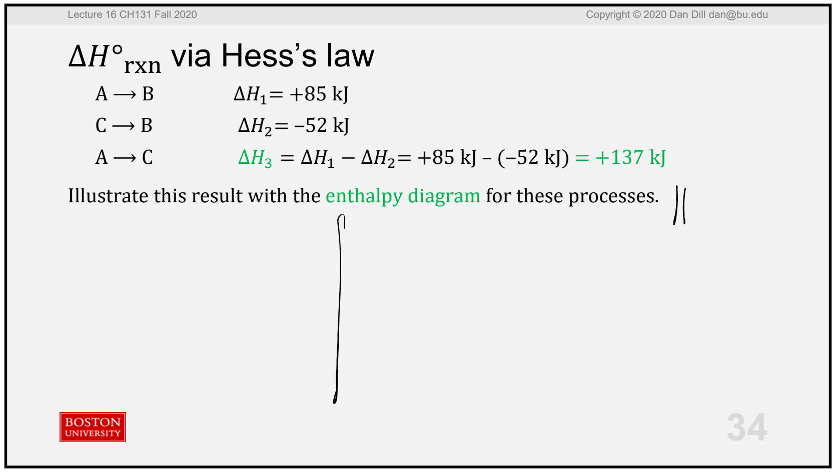
$A \longrightarrow B$ $\Delta H_1 = +85\ \text{kJ}$

$C \longrightarrow B$ $\Delta H_2 = -52\ \text{kJ}$

$A \longrightarrow C$ $\Delta H_3 = ?$

Since energy is conserved ...

$\Delta H_3 = \underline{\Delta H_1} - \Delta H_2 = \underline{+85\ \text{kJ} - (-52\ \text{kJ})} = +137\ \text{kJ}$



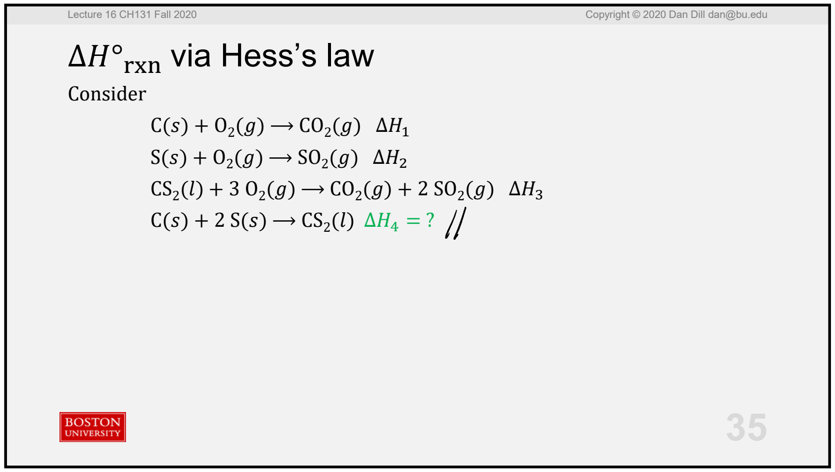
$\Delta H°_{\text{rxn}}$ via Hess's law

$A \longrightarrow B$ $\Delta H_1 = +85\ \text{kJ}$

$C \longrightarrow B$ $\Delta H_2 = -52\ \text{kJ}$

$A \longrightarrow C$ $\Delta H_3 = \Delta H_1 - \Delta H_2 = +85\ \text{kJ} - (-52\ \text{kJ}) = +137\ \text{kJ}$

Illustrate this result with the enthalpy diagram for these processes.



$\Delta H°_{\text{rxn}}$ via Hess's law

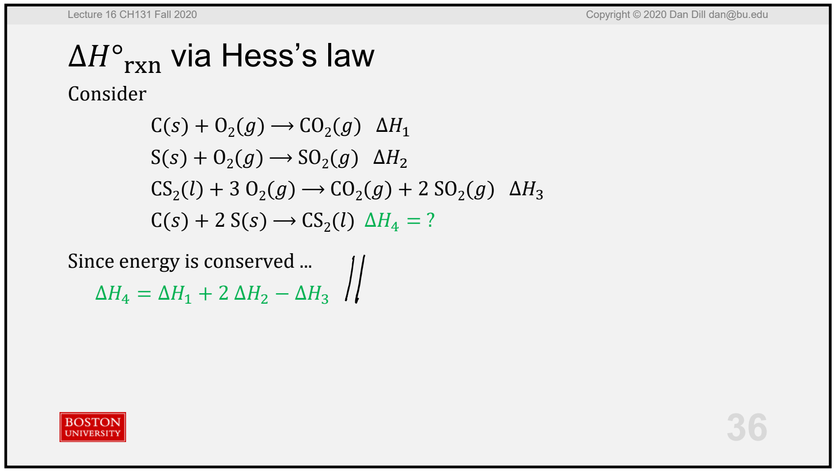
Consider

$C(s) + O_2(g) \longrightarrow CO_2(g)$ ΔH_1

$S(s) + O_2(g) \longrightarrow SO_2(g)$ ΔH_2

$CS_2(l) + 3\ O_2(g) \longrightarrow CO_2(g) + 2\ SO_2(g)$ ΔH_3

$C(s) + 2\ S(s) \longrightarrow CS_2(l)$ $\Delta H_4 = ?$



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$\Delta H°_{\mathrm{rxn}}$ via Hess's law

Consider

$C(s) + O_2(g) \longrightarrow CO_2(g)$ ΔH_1

$S(s) + O_2(g) \longrightarrow SO_2(g)$ ΔH_2

$CS_2(l) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,SO_2(g)$ ΔH_3

$C(s) + 2\,S(s) \longrightarrow CS_2(l)$ $\Delta H_4 = ?$

Since energy is conserved …

$\Delta H_4 = \Delta H_1 + 2\,\Delta H_2 - \Delta H_3$

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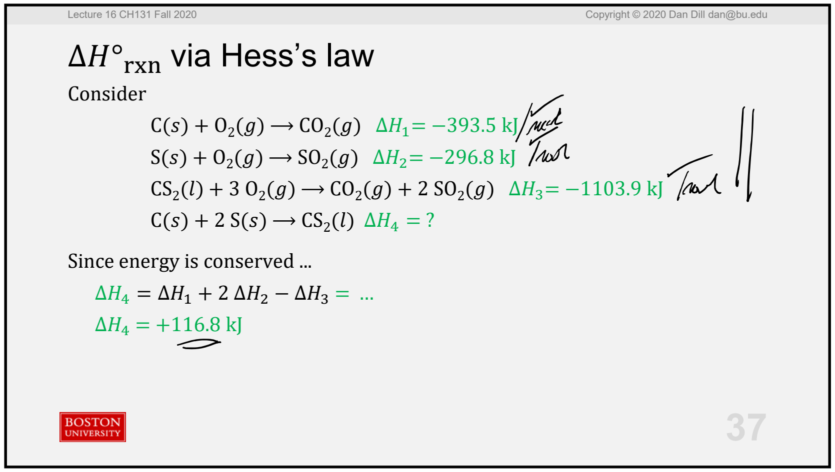

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$\Delta H°_{\mathrm{rxn}}$ via Hess's law

Consider

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H_1 = -393.5$ kJ /mol

$S(s) + O_2(g) \longrightarrow SO_2(g)$ $\Delta H_2 = -296.8$ kJ /mol

$CS_2(l) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,SO_2(g)$ $\Delta H_3 = -1103.9$ kJ /mol

$C(s) + 2\,S(s) \longrightarrow CS_2(l)$ $\Delta H_4 = ?$

Since energy is conserved …

$\Delta H_4 = \Delta H_1 + 2\,\Delta H_2 - \Delta H_3 = \ldots$

$\Delta H_4 = +116.8$ kJ

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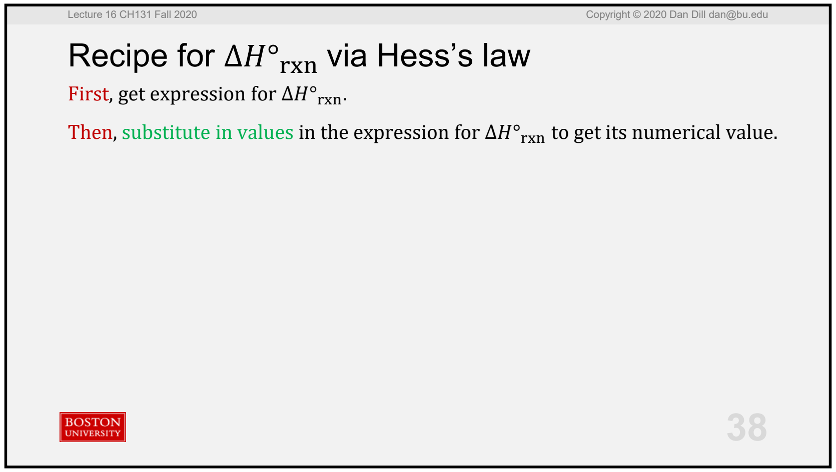

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Recipe for $\Delta H°_{\mathrm{rxn}}$ via Hess's law

First, get expression for $\Delta H°_{\mathrm{rxn}}$.

Then, substitute in values in the expression for $\Delta H°_{\mathrm{rxn}}$ to get its numerical value.

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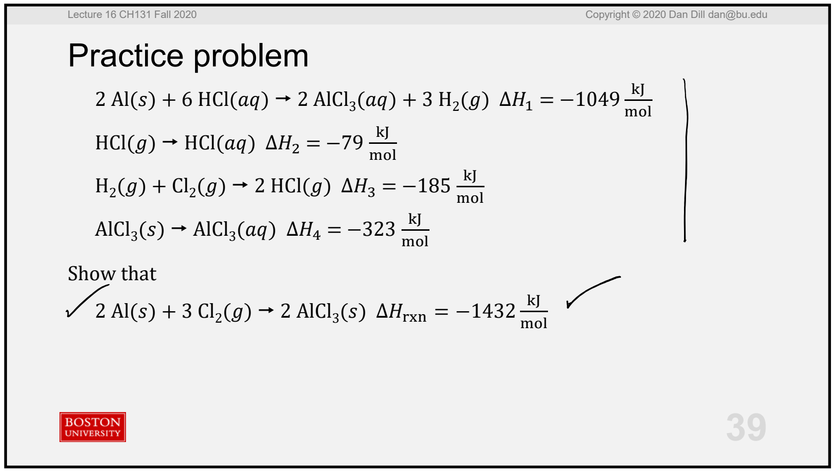

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Practice problem

$2\,Al(s) + 6\,HCl(aq) \rightarrow 2\,AlCl_3(aq) + 3\,H_2(g)$ $\Delta H_1 = -1049\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

$HCl(g) \rightarrow HCl(aq)$ $\Delta H_2 = -79\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ $\Delta H_3 = -185\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

$AlCl_3(s) \rightarrow AlCl_3(aq)$ $\Delta H_4 = -323\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

Show that

✓ $2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$ $\Delta H_{\mathrm{rxn}} = -1432\,\frac{\mathrm{kJ}}{\mathrm{mol}}$ ✓

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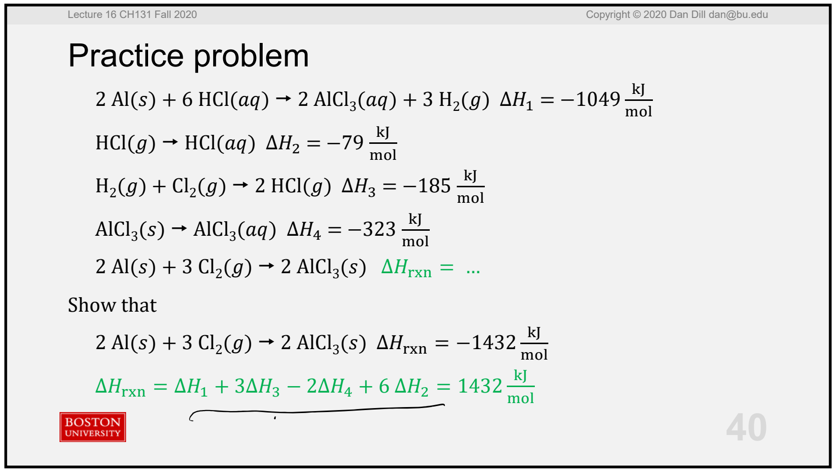


Practice problem

$2\,Al(s) + 6\,HCl(aq) \rightarrow 2\,AlCl_3(aq) + 3\,H_2(g)\ \ \Delta H_1 = -1049\,\frac{kJ}{mol}$

$HCl(g) \rightarrow HCl(aq)\ \ \Delta H_2 = -79\,\frac{kJ}{mol}$

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)\ \ \Delta H_3 = -185\,\frac{kJ}{mol}$

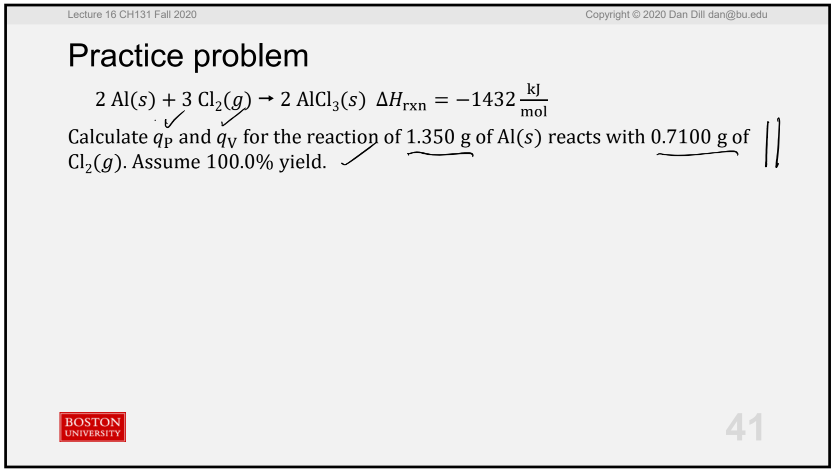
$AlCl_3(s) \rightarrow AlCl_3(aq)\ \ \Delta H_4 = -323\,\frac{kJ}{mol}$

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = \ldots$

Show that

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

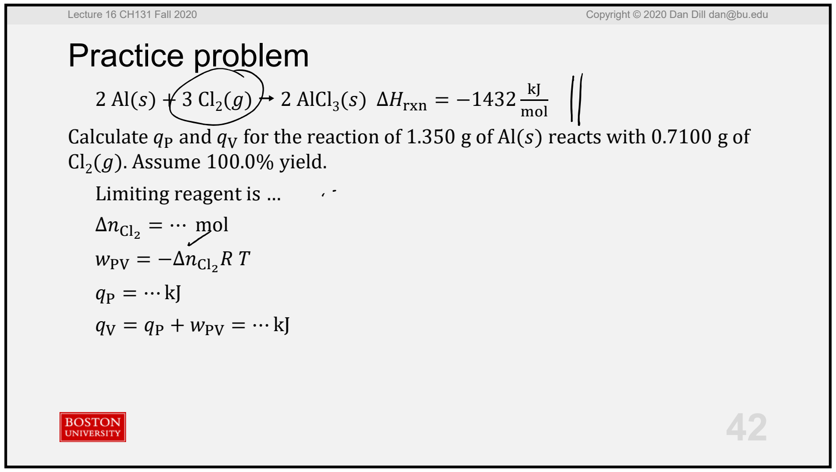
$\Delta H_{rxn} = \underbrace{\Delta H_1 + 3\Delta H_3 - 2\Delta H_4 + 6\,\Delta H_2}_{} = 1432\,\frac{kJ}{mol}$



Practice problem

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

Calculate q_P and q_V for the reaction of $\underbrace{1.350\text{ g}}$ of $Al(s)$ reacts with $\underbrace{0.7100\text{ g}}$ of $Cl_2(g)$. Assume 100.0% yield.



Practice problem

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

Calculate q_P and q_V for the reaction of 1.350 g of $Al(s)$ reacts with 0.7100 g of $Cl_2(g)$. Assume 100.0% yield.

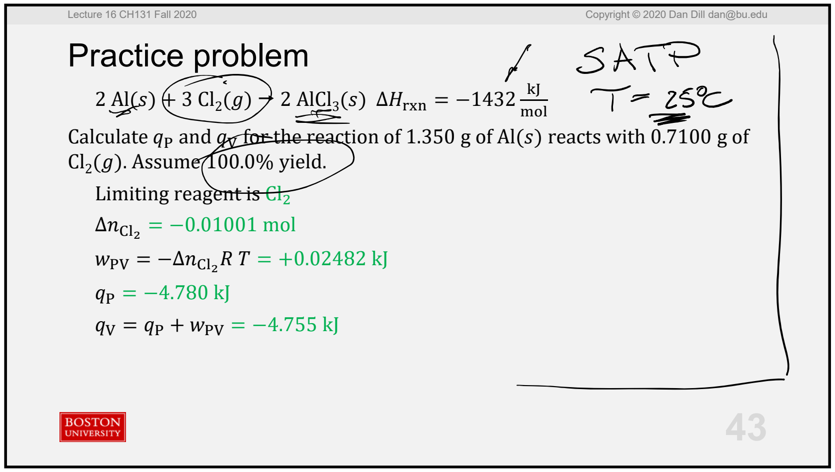
Limiting reagent is …

$\Delta n_{Cl_2} = \cdots$ mol

$w_{PV} = -\Delta n_{Cl_2} R\,T$

$q_P = \cdots$ kJ

$q_V = q_P + w_{PV} = \cdots$ kJ



Practice problem

SATP

T = 25°C

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)\ \ \Delta H_{rxn} = -1432\,\frac{kJ}{mol}$

Calculate q_P and q_V for the reaction of 1.350 g of $Al(s)$ reacts with 0.7100 g of $Cl_2(g)$. Assume 100.0% yield.

Limiting reagent is Cl_2

$\Delta n_{Cl_2} = -0.01001$ mol

$w_{PV} = -\Delta n_{Cl_2} R\,T = +0.02482$ kJ

$q_P = -4.780$ kJ

$q_V = q_P + w_{PV} = -4.755$ kJ