# Predicting effect of work on heat

CH101 Fall 2014

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**Heat depends on whether there is work**

**$\Delta U = q_V$ can be different from $\Delta H = q_P$**

**Express this in a sentence, without using symbols or jargon**



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## Heat depends on whether there is work

The reaction

$NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$

is **endothermic, q > 0** (solution/surroundings **cool**).

**How much cooling** is there at constant volume ($q_V$) **compared to** that at constant pressure ($q_P$)?

**Let's learn how to predict what we expect…**



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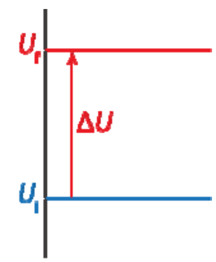
## Heat depends on whether there is work

The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings **cool**). Sketch **the energy diagram** for this reaction: Indicate the initial and final energy by horizontal lines labeled $U_i$ and $U_f$, respectively, and connect the lines by an arrow labeled $\Delta U$.



[TP] The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings cool). **How will $U_i$ change** depending on whether the reaction is run in a sealed flask (constant V) or an open flask (constant P)?

33% 1. $U_i$ change will not change
33% 2. $U_i$ change will change depending on work $w$
33% 3. Cannot know without further information

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[TP] The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings cool). **How will $U_f$ change** depending on whether the reaction is run in a sealed flask (constant V) or an open flask (constant P)?

33% 1. $U_f$ change will not change
33% 2. $U_f$ change will change depending on work $w$
33% 3. Cannot know without further information

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[TP] The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings cool). **How will $\Delta U$ change** depending on whether the reaction is run in a sealed flask (constant V) or an open flask (constant P)?

33% 1. $\Delta U$ will not change
33% 2. $\Delta U$ will change depending on work $w$
33% 3. Cannot know without further information

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## Heat depends on whether there is work

The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings **cool**). Since $U_i$ and $U_f$, are not affected by how the reaction is carried out…

- $\Delta U$ is **always the same** for a given reaction
- $\Delta U$ is like a social security number of the reaction; **it never changes**

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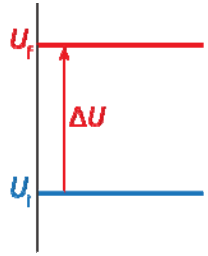
The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings **cool**). Assume that the flask is **sealed**, so that gas generated **cannot escape**, and so no work is done ($w = 0$).

Add an arrow to the energy diagram corresponding to $q_V$.





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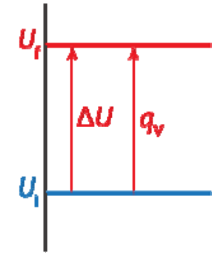




 

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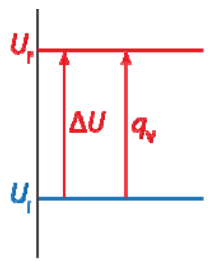
Based on your $q_V$ arrow, what is the relation between $\Delta U$ and $q_V$?





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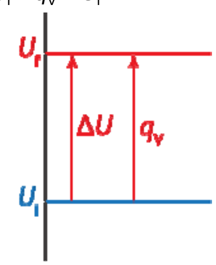
Since $U_i + q_V$ ends at $U_f$, $U_i + q_V = U_f$ …

$U_f - U_i = \mathbf{\Delta U = q_V}$





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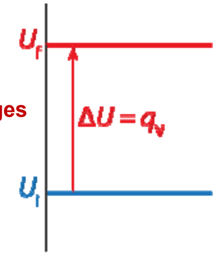
Since $U_i + q_V$ ends at $U_f$, $U_i + q_V = U_f$ …

$U_f - U_i =$ **$\Delta U = q_V$**

The value of $q_V$ ***is*** $\Delta U$

For a given reaction …

$\Delta U = q_V$ **never changes**





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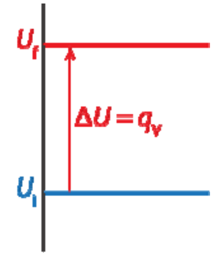
Draw a new energy diagram showing just $U_i$, $U_f$, and $\Delta U = q_V$.





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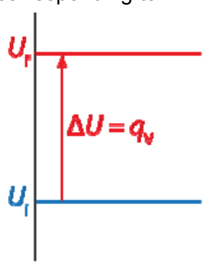
Add an arrow starting at $U_i$ corresponding to $w$.





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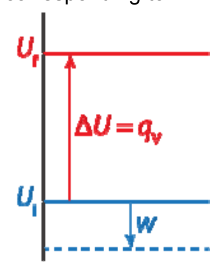




 

 

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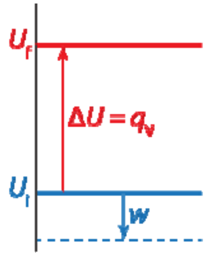
At what value of $U$ does the $w$ arrow end?

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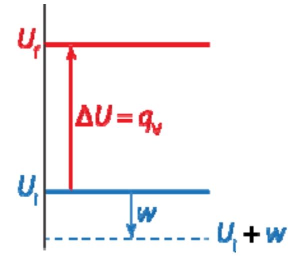
At what value of $U$ does the $w$ arrow end?

$U_i + w$

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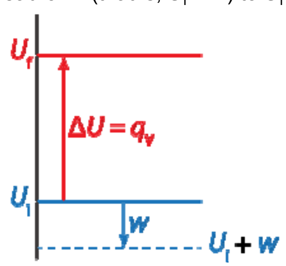
Draw an **arrow *a*** from the head of $w$ (that is, $U_i + w$) to $U_f$

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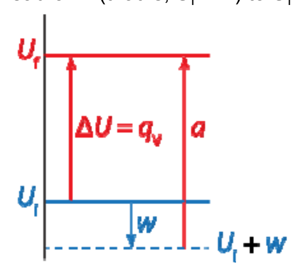


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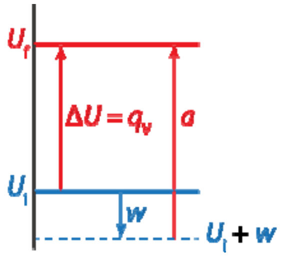
Use the first law to determine the **length of the arrow *a***.

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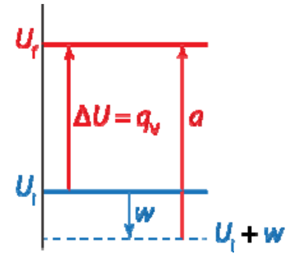
The **length of the arrow *a*** is …

$a$ = head – tail

$= U_f - (U_i + w)$

$= U_f - U_i - w$

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The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings **cool**). Assume that the flask is **open**, so that gas generated **can escape**, and so that **work is done** by the released $CO_2$ (**w < 0**).

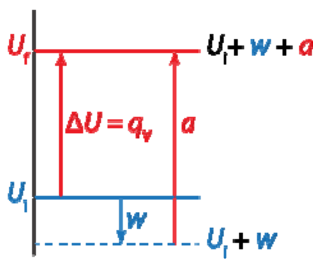
The **length of the arrow *a*** is …

$a$ = head – tail

$= U_f - (U_i + w)$

$= U_f - U_i - w$

$= \Delta U - w$

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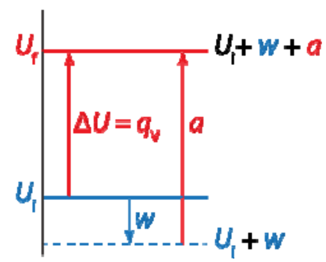
The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings **cool**). Assume that the flask is **open**, so that gas generated **can escape**, and so that **work is done** by the released $CO_2$ (**w < 0**).

Since $a = \Delta U - w$ and $\Delta U = q + w$ …

$a = q + w - w$

$= q$ in the open flask




24

## Heat depends on whether there is work

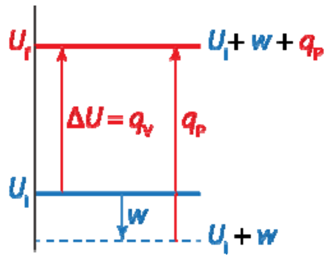
The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings **cool**). Assume that the flask is **open**, so that gas generated **can escape**, and so that **work is done** by the released $CO_2$ (**w < 0**).

Since $a = \Delta U - w$ and $\Delta U = q + w$ …

$a = q + w - w$

$= q$ in the open flask

$= q_P$

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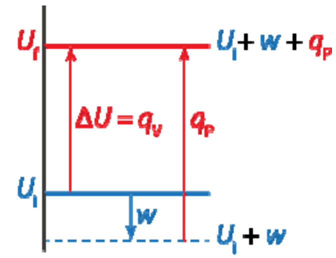
## Heat depends on whether there is work

The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is **endothermic, q > 0** (solution/surroundings **cool**). Comparing your two energy diagrams, make a prediction about how much cooling there is when the flask is sealed **compared to** when the flash is open.

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[TP] The reaction $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ is endothermic, q > 0 (solution/surroundings cool). **Comparing your two energy diagrams**, make a prediction about how much cooling there is when the flask is sealed (constant volume) **compared to** when the flash is open (constant pressure).

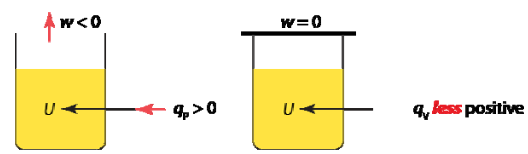
25% 1. Cooling is **smaller** at constant volume, $q_V < q_P$
25% 2. Cooling is **the same** at constant volume, $q_V = q_P$
25% 3. Cooling is **greater** at constant volume, $q_V > q_P$
25% 4. Unable to know without further information

Response Counter 10

27

## Heat depends on whether there is work




**Endothermic** reaction that does **work on surroundings** will get **less cold** at constant volume.

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## Heat depends on whether there is work

The reaction

$NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$

is **endothermic, q > 0** (solution/surroundings **cool**).

**How much cooling** is there at constant volume ($q_V$) **compared to** that at constant pressure ($q_P$)?

**Let's measure to see…**

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## Heat depends on whether there is work

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ is exothermic, q > 0 (solution/surroundings warm). Sketch the two energy diagrams for this process, once for a sealed flask, one for an open flask.

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[TP] $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ is exothermic, q > 0 (solution/surroundings warm). Based on the energy diagrams, how much warming is there at **constant volume** ($q_V$), compared to that at constant pressure ($q_P$)?

25% 1. Warming is **greater** at constant volume, $|q_V| > |q_P|$
25% 2. Warming is **the same** at constant volume, $|q_V| = |q_P|$
25% 3. Warming is **smaller** at constant volume, $|q_V| < |q_P|$
25% 4. Unable to know without further information

Response Counter 10

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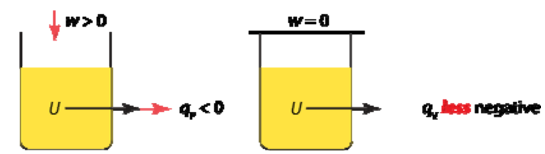
## Heat depends on whether there is work




**Exothermic** reaction that has **work done on it** will get **less hot** at constant volume.

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# Heat depends on whether there is work

What we have learned …

$\Delta U$ never changes for a reaction, whether there is work or not. Its numerical value is $q_V$, the heat were the process to be carried out in a sealed, rigid container (constant volume).

If no work is present, then $\Delta U = q = q_V$

If work is present, construct the energy diagram connecting $U_i$ and $U_f$ for the process, to determine how $q = q_P = \Delta H$ compares to $q_V = \Delta U$

For a worked example, see CH101 A3 lecture 17 at **http://quantum.bu.edu/courses/ch101/lectures.html**

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