

Lecture 23 CH101 A2 (MWF 11:15 am) Fall 2018 Copyright © 2016 Dan Dill dan@bu.edu

[TP] Consider the reaction  $2 \text{H}_2\text{O}(l) + 3 \text{CH}_4(g) + \text{CO}_2(g) \rightleftharpoons 4 \text{CH}_3\text{OH}(l)$ .  
This **chemical system** must be ...

20% 1. doing work and so  $w > 0$   
20% 2. doing work and so  $w < 0$   
20% 3. having work done on it and so  $w > 0$   
20% 4. having work done on it and so  $w < 0$   
20% 5. Further information needed

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Lecture 23 CH101 A2 (MWF 11:15 am)  
Wednesday, October 31, 2018

For today ...

- Detecting work
- Amount of heat depends on whether there is work

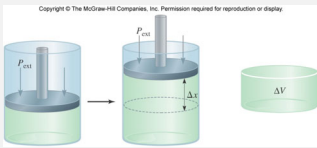
Next lecture: Continue: Amount of heat depends on whether there is work

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### How do we know if work is present?

Macroscopic movement, for example a piston.



Work done **by** gas: force  $\times$  distance  $= (F / A) \times (\Delta x A) = P_{\text{ext}} \Delta V$   
Work done **on** gas:  $w = -P_{\text{ext}} \Delta V$

Expansion of gas **pushes** against  $P_{\text{ext}}$ , gas **expends** energy,  $w < 0$   
Compression of gas **pushed on** by  $P_{\text{ext}}$ , gas **gains** energy,  $w > 0$

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**[Quiz]** When  $\text{NaHCO}_3(s)$  is dissolved in 200 mL of  $\text{HCl}(aq)$ ,  $\text{CO}_2(g)$  bubbles form. This means the chemical reaction between the  $\text{NaHCO}_3(s)$  and the  $\text{HCl}(aq)$  must be ...

- 20% 1. doing work and so  $w > 0$
- 20% 2. doing work and so  $w < 0$
- 20% 3. having work done on it and so  $w > 0$
- 20% 4. having work done on it and so  $w < 0$
- 20% 5. Further information needed



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The amount of heat depends on whether there is work

$$\Delta U = q_V \text{ can be different from } \Delta H = q_P$$

Complete this sentence: If you carry out a reaction in a sealed, rigid container the heat ...



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## Heat depends on whether there is work

The reaction



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 carry out the reaction to see.



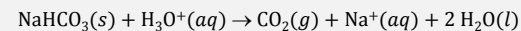
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## Heat depends on whether there is work

The reaction



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 the difference between  $q_V$  and  $q_P$ .



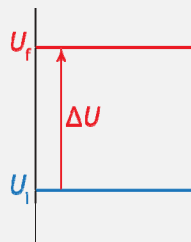
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### Heat depends on whether there is work

The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  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  $\Delta U$ .

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**[TP]** The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  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  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  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  
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**[Quiz]** The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  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  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  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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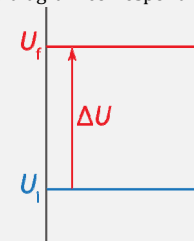
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## Heat depends on whether there is work

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



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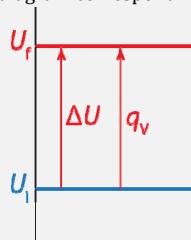
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The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  is endothermic,  $q > 0$  (solution/surroundings **cool**). Assume that the flask is **sealed**, so that gas generated **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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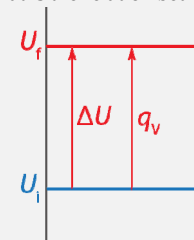
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The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  is endothermic,  $q > 0$  (solution/surroundings **cool**). Assume that the flask is **sealed**, so that gas generated **cannot escape**, and so no work is done ( $w = 0$ ).

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



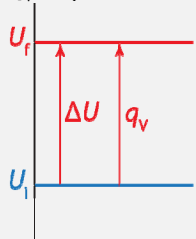
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### Heat depends on whether there is work

The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  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 ( $w = 0$ ).

Since  $U_i + q_v$  ends at  $U_f$ ,  $U_i + q_v = U_f$  ...

$$U_f - U_i = \Delta U = q_v$$


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### Heat depends on whether there is work

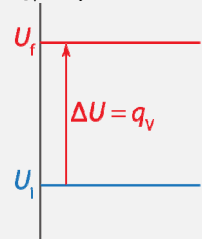
The reaction  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  is endothermic,  $q > 0$  (solution/surroundings **cool**). Assume that the flask is **sealed**, so that gas generated **cannot escape**, and so no work is done ( $w = 0$ ).

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 ...

$$\Delta U = q_v \text{ never changes}$$


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