

Lecture 24 CH101 A1 (MWF 9:05 am) Fall 2017

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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). 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 flask 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



1

## Lecture 24 CH101 A1 (MWF 9:05 am)

Friday, November 3, 2017

## For today ...

- Complete: Amount of heat depends on whether there is work

Next lecture: Temperature equilibration; Heating curves; Enthalpy change of reaction,  $\Delta_r H$ ; [ Calorimetry, pp 231–232, done in lab ]; Hess's law; Standard states and standard  $\Delta_r H$ ; Standard enthalpy of formation,  $\Delta_f H^\circ$ ; using  $\Delta_f H^\circ$  to compute any  $\Delta_r H$ ; bond enthalpies,  $\Delta_b H$ ; Using  $\Delta_b H$  to estimate  $\Delta_r H$ .



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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).



3

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How much cooling is there at constant volume ( $q_v$ ) compared to that at constant pressure ( $q_p$ )?

Let's measure to see...



4

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

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The **length of the arrow  $a$**  is ...

$a = \text{head} - \text{tail}$   
 $= U_f - (U_i + w)$   
 $= U_f - U_i - w$

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The **length of the arrow  $a$**  is ...

$a = \text{head} - \text{tail}$   
 $= U_f - (U_i + w)$   
 $= U_f - U_i - w$   
 $= \Delta U - w$

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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 **open**, so that gas generated **can escape**, and so that **work is done** by the released  $\text{CO}_2$  ( $w < 0$ ).

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

$a = q + w - w$   
 $= q$  in the open flask

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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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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). Comparing your two energy diagrams, make a prediction about how much cooling there is when the flask is sealed compared to when the flask is open.

$U_i$   $U_i + w + q_p$   $U_i + w$

$\Delta U = q_v$   $q_p$   $w$

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25% 4. Unable to know without further information

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### Heat depends on whether there is work

$w < 0$   $w = 0$

$U$   $U$   $q_p > 0$   $q_p$  less positive

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

$\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$  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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[Quiz]  $\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$  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



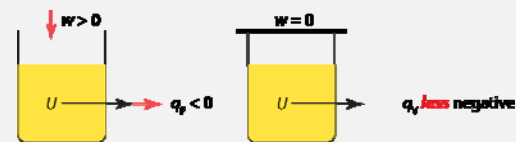
Response Counter

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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.



22

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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.

The numerical value of  $\Delta U$  is  $q_v$ , the heat were the process to be carried out in a sealed, rigid container (constant volume).

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  $q_v = \Delta U$ .



23