

Lecture 24 CH101 A1 (MWF 9 am) Fall 2016 Copyright © 2016 Dan Dill dan@bu.edu

[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). 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

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Response Counter 10 1

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Friday, November 4, 2016

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

Next lecture: Temperature equilibration (heat leveling); heating curves; enthalpy change of reaction, $\Delta_r H$; [Calorimetry, pp 231–232, done in lab]

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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...

ΔU is **always the same** for a given reaction
 ΔU is **like a social security number** of the reaction; **it never changes**

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Add an arrow to the energy diagram corresponding to q_V .

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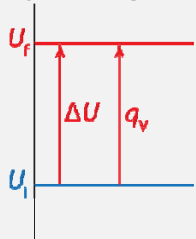
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The reaction $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$ is endothermic, $q > 0$ (solution/surroundings **cool**). Assume that the flask is **sealed**, so that gas generated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

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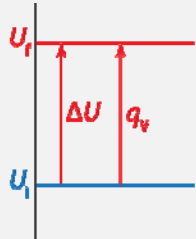
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Heat depends on whether there is work

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 ($w = 0$).

Based on your q_v arrow, what is the relation between ΔU and q_v ?



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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 ($w = 0$).

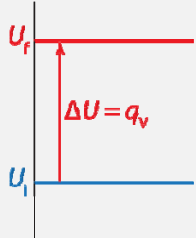
Since $U_i + q_v$ ends at U_f , $U_i + q_v = U_f$...

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

The value of q_v is ΔU

For a given reaction ...

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



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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**).

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

Let's measure to see ...

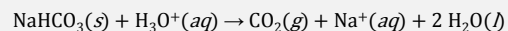
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Heat depends on whether there is work

Analysis of experiments



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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**). How would your energy diagram change if the flask were open?



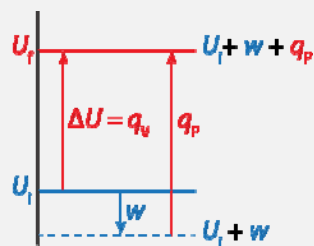
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Heat depends on whether there is work

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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, $q_v > q_p$
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Response Counter

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Can w change the sign of q ?

Answer: In principle yes; in practice, no.

w is always very small compared with q_v ,
and so q_p always has the same sign as q_v .



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Heat depends on whether there is work

The combustion $\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$ 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] Combustion $\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$ 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



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Heat depends on whether there is work

What we have learned ...

ΔU **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).

$\Delta U = q_v$ always.

$\Delta H = q_p$ always.

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 $q_v = \Delta U$



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