# Thermochemistry

Massachusetts Insight Workshop November 10, 2020

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### Welcome to the Session on Thermochemistry

- We will begin this afternoon with some vocabulary and some questions to gain some idea of your intuition about heat, mass and change in temperature (ΔT).
- Heat is measured in units of joules (J) or kilojoules (kJ). Heat is one of two ways energy is transferred.
- Mass is measured in unit of grams.
- Temperature is measured in units of degrees Celsius (°C). Temperature is a measure of the average kinetic energy of a sample of matter.

1. Consider the two beakers containing water, both at the same initial temperature, say 25 degrees Celsius.



The beaker on the left has 25 mLs of water and the beaker on the right has 50 mLs of water. Both have the same initial temperature. If the same amount of heat is added to both beakers, using a bunsen burner, does the beaker on the right or the beaker on the left have the higher final temperature?

right or left

1. Consider the two beakers containing water, both at the same initial temperature, say 25 degrees Celsius.



The beaker on the left has 25 mLs of water and the beaker on the right has 50 mLs of water. Both have the same initial temperature. If the same amount of heat is added to both beakers, using a bunsen burner, does the beaker on the right or the beaker on the left have the higher final temperature?

right or left

In this experiment q (amount of heat) is constant. What is the relationship between mass and change in temperature?





2. Consider the two beakers containing water, both at the same initial temperature, say 25 degrees Celsius.



If the final temperature of the water in both beakers is identical, is the greater amount of heat added to the beaker on the right or the beaker on the left?

right or left

2. Consider the two beakers containing water, both at the same initial temperature, say 25 degrees Celsius.



If the final temperature of the water in both beakers is identical, is the greater amount of heat added to the beaker on the right or the beaker on the left?

right or left

In this experiment  $\Delta T$  (change in temperature) is constant. What is the relationship between heat and mass?



- In the two experiments we have considered we know the following relationships between heat, mass and change in temperature:
- Experiment #1 :
- Experiment #2 :



3. Consider two beakers each with the same volume of water at the same initial temperature,25°C.



If twice the heat was added to the beaker on the right compared to the beaker on the left, does the beaker on the right or on the left have the highest final temperature?



**Right or left** 

3. Consider two beakers each with the same volume of water at the same initial temperature,25°C.



If twice the heat was added to the beaker on the right compared to the beaker on the left, does the beaker on the right or on the left have the highest final temperature?



In this experiment mass is constant. What is the relationship between heat and  $\Delta T$ ?

DCI15.1. Two containers of water are at 20 °C initially. One contains 50 mLs and the other 100 mLs. They are each heated with the same source of heat for the same amount of time. If the final temperature of the 50 mLs sample is 50 °C what would be the final temperature of the 100 mLs sample?

A.	50 °C
B.	80 °C
C.	25 °C
D.	100 °C
E.	35 °C

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A.	50 °C	Same amount of heat
B.	80 °C	to both beakers, but
C.	25 °C	different mass. $\Delta T =$
с.	20 0	30° for beaker on the
D.	100 °C	left, so $\Delta T$ is half or 15°.
E.	35 °C	

#### Mass $\alpha$ 1/ $\Delta$ T



Two containers each have 50 mLs of water at 20 °C initially. They are each heated with the same source of heat. One is heated for ten minutes and the other for five minutes. If the container that was heated for five minutes has a final temperature 30 °C what would be the final temperature of the other sample?

A.	35 °C
B.	40 °C
C.	60 °C
D.	25 °C
E.	30 °C



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A.	35 °C	Both beakers contain the
R	40 °C	same amount of water.
<b>D</b> .		Twice the heat to one. $\Delta T$
C.	60 °C	is 10° for smaller amount
D.	25 °C	of heat, than $\Delta T = 20^{\circ}$ for
E.	30 °C	larger amount.

Q(heat)  $\alpha \Delta T$ 



Two containers of water are at 20 °C initially. One contains 50 g of water and is heated by a source for a specified time to a final temperature of 30 °C. The second container has an unknown amount of water and is heated with the same source to 30 °C. However, it takes twice as long to get to this final temperature. How much water is in this container?

- A. 100 g
- B. 25 g
- C. 30 g
- D. 50 gE. 75 g



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<b>A.</b>	<b>100 g</b>	Twice the heat is added to
B.	25 g	one beaker to reach the
C.	30 g	$(\Delta T)$ . So the beaker must
D.	50 g	have twice the mass.
E.	75 g	



Q(heat)  $\alpha$  Mass

So we have established the following relationships;

> Mass  $\alpha$  1/ $\Delta$ T q(heat)  $\alpha \Delta T$  at constant mass q(heat)  $\alpha$  mass at constant  $\Delta T$

at constant q

So

q(heat)  $\alpha$  mass  $\cdot \Delta T$ 

Heat is directly proportional to the mass times the change in temperature.

















q(heat)  $\alpha$  mass  $\cdot \Delta T$ 

How do we make this an equality?

We must introduce a constant....in this case the constant is called the specific heat, SH,

 $q(heat) = mass \cdot SH \cdot \Delta T$ 

Specific heat is the amount of heat required to raise the temperature of 1 gram of a substance 1 °C.

Specific Heats of Substances

Compound	Specific Heat
	(J °C <sup>-1</sup> g <sup>-1</sup> )
H <sub>2</sub> O(I)	4.184
$H_2O(s)$	2.03
Al(s)	0.89
C(s)	0.71
Fe(s)	0.45
Hg(I)	0.14
O <sub>2</sub> (g)	0.917
CH <sub>3</sub> CH <sub>2</sub> OH	2.46

Specific Heats of Substances

Exp	Heat Added (J)	Mass (g)	T <sub>i</sub> (°C)	T <sub>f</sub> (°C)	
1	1000	10.0	20.0	43.9	
2	2000	10.0	20.0	67.8	
3	3000	10.0	20.0	91.7	
4	1000	20.0	20.0		
5	1700	45.0	25.0		

Note: All five experiments use the same substance.

Specific Heats of Substances

Exp	Heat	Mass	T <sub>i</sub>	T <sub>f</sub>	ΔΤ	Constant
	Added (J)	(g)	(°C)	(°C)	(°C)	
1	1000	10.0	20.0	43.9	23.9	4.184
2	2000	10.0	20.0	67.8	47.8	4.184
3	3000	10.0	20.0	91.7	71.7	4.184
4	1000	20.0	20.0	32.0	12.0	4.184
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- In the three experiments we have considered we know the following relationships between heat, mass and change in temperature:
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Very important relationship

 $q = mass \cdot c \cdot \Delta T$ 

c has units of joules  $\cdot \ g^{\text{-1}} \cdot \ ^\circ \text{C}^{\text{-1}}$ 

#### DANGER!!

We must be very careful using this relationship!

Calculates the magnitude of the heat released or absorbed but not the sign of q.

Using

 $q = mass \cdot c \cdot \Delta T$ 

To calculate the magnitude of the heat released or absorbed but not the sign of q.

For example, an exothermic reaction in water will cause the aqueous solution to increase in temperature so  $T_{final}$  is larger than  $T_{initial}$  and  $\Delta T$  would be a positive number. The mass of the solution and the specific heat of the solution are also positive, so using the equation q = mass  $\cdot c \cdot \Delta T$  to calculate q yields a positive value for q! For exothermic reactions q must be negative.

**First Law of Thermodynamics** 

Experiments that we do in AP chemistry.

Mix hot and cold water

Add a hot piece of metal to water at room temperature

Add an ionic solid to water

Mix a strong acid with a strong base Mix a strong acid with a reactive metal

**First Law of Thermodynamics** 

Experiments that we do in AP chemistry.

Mix hot and cold water; Add a hot piece of metal to water at room temperature; Add an ionic solid to water;

Mix a strong acid with a strong base ; Mix a strong acid with a reactive metal; qhot water = -qcold water
qhot metal = -qcold water
qdissolution = -qsolution

q<sub>neutralization</sub> = -q<sub>solution</sub> q<sub>reaction</sub> = -q<sub>solution</sub>

 $MgO(s) + 2 H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$ 

3. A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net-ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume of 1.0 M HCl (mL)	Mass of MgO(s) Added (g)	Initial Temperature of Solution (°C)	Final Temperature of Solution (°C)
1	100.0	0.25	25.5	26.5
2	100.0	0.50	25.0	29.1
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(a) Which is the limiting reagent in all four trials, HCl or MgO? Justify your answer.

(b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

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For parts (c) and (d), use the data from one of the other three trials (i.e., not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is  $4.18 \text{ J/(g}^{\circ}\text{C})$ . Assume that the density of the HCl(aq) is 1.0 g/mL.

(c) Calculate the magnitude of q, the thermal energy change, when the MgO was added to the 1.0 M HCl(aq). Include units with your answer.

(d) Determine the student's experimental value of ΔH° for the reaction between MgO and HCl in units of kJ/mol<sub>rxn</sub>.

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 $q_{rxn} = -q_{solution} = -(mass \cdot c \cdot \Delta T)_{solution}$ 

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(d) Determine the student's experimental value of  $\Delta H^{\circ}$  for the reaction between MgO and HCl in units of kJ/mol<sub>rxn</sub>.

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(Using Trial 2 data)  $\Delta H_{rxn} = q_{rxn} / mol_{rxn}$ 

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(e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of  $\Delta H^{\circ}$  for the reaction between MgO(s) and HCl(aq).

Substance	∆H° <sub>f</sub> (kJ/mol)
MgO(s)	-602
$H_2O(l)$	-286
H⁺(aq)	0
Mg <sup>2+</sup> (aq)	-467

### AP Chemistry Exam Equations for Thermochemistry

#### THERMODYNAMICS/ELECTROCHEMISTRY

 $q = mc\Delta T$   $\Delta S^{\circ} = \sum S^{\circ} \text{ products} - \sum S^{\circ} \text{ reactants}$   $\Delta H^{\circ} = \sum \Delta H_{f}^{\circ} \text{ products} - \sum \Delta H_{f}^{\circ} \text{ reactants}$   $\Delta G^{\circ} = \sum \Delta G_{f}^{\circ} \text{ products} - \sum \Delta G_{f}^{\circ} \text{ reactants}$   $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$   $= -RT \ln K$   $= -nFE^{\circ}$   $I = \frac{q}{t}$  $E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln Q$ 



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 $\Delta H^{\circ}_{rxn}$  = -151 kJ/1 mol <sub>rxn</sub>

 $Na_2S_2O_3(aq) + 4 NaOCl(aq) + 2 NaOH(aq) \rightarrow 2 Na_2SO_4(aq) + 4 NaCl(aq) + H_2O(l)$ 

1. A student performs an experiment to determine the value of the enthalpy change,  $\Delta H^{\circ}_{rxn}$ , for the oxidation-reduction reaction represented by the balanced equation above.

In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (M)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	5
NaOCl(aq)	0.500	5
NaOH(aq)	0.500	5

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$Na_2S_2O_3(aq)$	0.500	5
NaOCl(aq)	0.500	5
NaOH(aq)	0.500	5

 $Na_2S_2O_3(aq) + 4 NaOCl(aq) + 2 NaOH(aq) \rightarrow 2 Na_2SO_4(aq) + 4 NaCl(aq) + H_2O(l)$ 

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The solutions, all originally at 20.0  $^{\circ}$ C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



(d) According to the graph, what is the temperature change of the reaction mixture?

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the reaction. Assume that the specific heat of the reaction mixture is  $3.94 \text{ J/(g} \cdot ^{\circ}\text{C})$  and that the heat absorbed by the calorimeter is negligible.

$$q_{rxn} = -q_{solution} = -(mass \cdot c \cdot \Delta T)_{solution}$$
  
 $q_{rxn} =$ 

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(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is  $3.94 \text{ J/(g} \cdot ^{\circ}\text{C})$  and that the heat absorbed by the calorimeter is negligible.

 $q_{rxn} = -q_{solution} = -(mass \cdot c \cdot \Delta T)_{solution}$  $q_{rxn} =$ 

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction,  $\Delta H^{\circ}_{rxn}$ , in kJ/mol<sub>rxn</sub>. Include the appropriate algebraic sign with your answer.

$$\Delta H_{rxn} = q_{rxn} / mol_{rxn} = \Delta H_{rxn} =$$

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(g) Write the balanced net ionic equation for the given reaction.



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 $HCNO(g) \rightleftharpoons HNCO(g)$ 

fulminic acid	isocyanic acid
Fulminic Acid	Isocyanic Acid
H−C≡N−Ö:	H—N=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of'  $\Delta H^{\circ}$  for the reaction of HCNO(g) to form HNCO(g).

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N-O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

### AP Chemistry Exam Equations for Thermochemistry

#### THERMODYNAMICS/ELECTROCHEMISTRY

 $q = mc\Delta T$   $\Delta S^{\circ} = \sum S^{\circ} \text{ products} - \sum S^{\circ} \text{ reactants}$   $\Delta H^{\circ} = \sum \Delta H_{f}^{\circ} \text{ products} - \sum \Delta H_{f}^{\circ} \text{ reactants}$   $\Delta G^{\circ} = \sum \Delta G_{f}^{\circ} \text{ products} - \sum \Delta G_{f}^{\circ} \text{ reactants}$   $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$   $= -RT \ln K$   $= -nFE^{\circ}$   $I = \frac{q}{t}$  $E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln Q$ 



### Mathematical Equations NOT on AP Chemistry Exam Equations Pages

 $\Delta H^{\circ}_{rxn} = \Sigma$  (Bond Energy(reactants)) -  $\Sigma$  (Bond Energy(products))



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