

## Lecture 9 CH131 Summer 1

Wednesday, June 5, 2019

- Postscript on osmotic pressure,  $\Pi = RTM_c$
- Ch12: Thermodynamic processes and thermochemistry
- Thermodynamic concepts
- Heat and work
- System and surrounding
- Heat depends on whether there is work, <http://goo.gl/1w80D0>

Next lecture: Enthalpy change of reaction,  $\Delta_r H$ . Hess's law. Standard enthalpy of formation of X,  $\Delta_f H^\circ(X)$ . Example thermochemistry problems



Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

Osmotic pressure  $\Pi = i c R T$ 

1.40 g of polyethylene ( $i = 1$ ) dissolved in 100. mL of benzene generates an osmotic pressure of 0.248 kPa at 25 °C. Calculate the molar mass of the polyethylene.

3. Calculate the molar mass...

$$1.40 \times 10^{-5} \text{ g/mol}$$

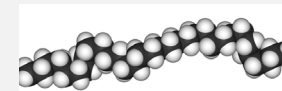
4. Calculate  $n$

$$M = n M(C_2H_4)$$

$$m = \frac{1.40 \times 10^{-5} \text{ g/mol}}{(2 \times 12.011 + 4 \times 1.008) \text{ g/mol}}$$

$$= 4990$$

For each molecule  
there are 2x4990 C atoms



2

Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

Osmotic pressure  $\Pi = i c R T$ 

1.40 g of polyethylene ( $i = 1$ ) dissolved in 100. mL of benzene generates an osmotic pressure of 0.248 kPa at 25 °C. Calculate the molar mass of the polyethylene.

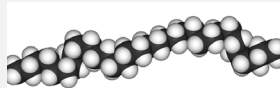
3. Calculate the molar mass...

$$1.40 \times 10^{-5} \text{ g/mol}$$

4. Calculate  $n$

$$n = 5347$$

$$2n = 10694 \text{ C atoms/molecule}$$



3

Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

[TP] 1.0 mg of a substance dissolved in 1.0 mL of water generates an osmotic pressure of 1.0 kPa, at 25 °C. The molar mass of the solute ( $i = 1$ ) is ...

- 31% 1. 250 g/mol  
0% 2. 500 g/mol  
6% 3. 1000 g/mol  
56% 4. 2500 g/mol  
0% 5. 5000 g/mol  
6% 6. Some other value

$$\textcircled{1} c = \frac{\Pi}{RT} = \frac{10^3 \text{ Pa}}{8.314 \text{ J/mol K} \times 300 \text{ K}}$$

$$= \frac{1}{2.5 \times 10^{-3} \text{ mol/L}}$$

$$\textcircled{2} cV = \frac{10^{-3} \text{ mol}}{2.5 \times 300 \text{ K}}$$

$$\textcircled{3} M = \frac{10^{-3} \text{ g}}{10^{-3} \text{ mol}} = 2.5 \times 300$$

$$= 750 \text{ g/mol}$$



4

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

Ch12: Thermodynamic processes and thermochemistry

BOSTON UNIVERSITY

5

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

### First law of thermodynamics

Energy,  $U$ , is **exchanged** between **system** and **surroundings** as **heat,  $q$** , and **work,  $w$** ,

$$\Delta U = q + w$$

**Positive values increase energy of system**

$$\Delta U = q + w$$

$q > 0$ : heat **flow into** the system  
 $w > 0$ : work **done on** the system

BOSTON UNIVERSITY

6

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

### How do we know heat is present?

Since  $q_{\text{sur}} = mc\Delta T_{\text{sur}}$  ...

we can use **temperature change of surroundings** to monitor **heat flow**.

BOSTON UNIVERSITY

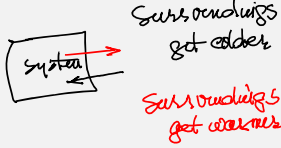
7

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

### How do we know heat is present?

Temperature **decrease in surroundings,  $\Delta T_{\text{sur}} < 0$**  means ...

energy flow **into system** from surroundings ...  
 energy of system goes up ...  
 and so,  $q > 0$ .



$q_{\text{sur}} = \text{mass}_{\text{sur}} \times \text{heat capacity}_{\text{sur}} \times \Delta T_{\text{sur}}$

BOSTON UNIVERSITY

8

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

## How do we know heat is present?

Temperature **increase in surroundings**,  $\Delta T_{\text{sur}} > 0$ , means ...  
 energy flow **out of system** into surroundings ...  
 energy of system goes down ...  
 and so,  $q < 0$ .

BOSTON UNIVERSITY 9

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] When  $\text{NaHCO}_3(\text{s})$  is dissolved in 200 mL of  $\text{HCl}(\text{aq})$ , the **temperature** of the solution **goes down**. This means the chemical reaction between the  $\text{NaHCO}_3(\text{s})$  and the  $\text{HCl}(\text{aq})$  results in the chemical system ...

0% 1. giving off heat and so  $q > 0$   
 29% 2. giving off heat and so  $q < 0$   
 0% 3. absorbing heat and so  $q < 0$   
 71% 4. absorbing heat and so  $q > 0$

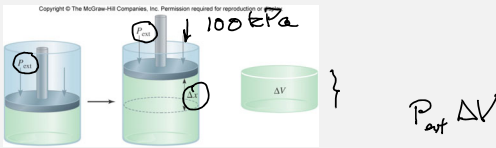
Usually, solution in which the rxn takes place is part of surroundings.

BOSTON UNIVERSITY 10

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

## How do we know if work is present?

Macroscopic movement, for example of 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,  $w > 0$

BOSTON UNIVERSITY 11

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

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

18% 1. doing work and so  $w > 0$   
 71% 2. doing work and so  $w < 0$   
 6% 3. having work done on it and so  $w > 0$   
 6% 4. having work done on it and so  $w < 0$

BOSTON UNIVERSITY 12

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

## Sign conventions for $q$ and $w$

Positive values increase energy of system  
 $\Delta U = q + w$   
 $q > 0$ : heat **flow into** the system (surroundings get colder)  
 $w > 0$ : work **done on** the system (volume of system ~~decreases~~ *increases*)

Direction of Energy Transfer	Sign Convention	Effect on $U_{\text{system}}$
Heat flow from <sup>colder</sup> surroundings to system	$q > 0 (+)$	$U$ increases, $\Delta U > 0$
Heat flow from system to <sup>warm</sup> surroundings	$q < 0 (-)$	$U$ decreases, $\Delta U < 0$
Work done on system by surroundings	$w > 0 (+)$	$U$ increases, $\Delta U > 0$
Work done on surroundings by system	$w < 0 (-)$	$U$ decreases, $\Delta U < 0$

BOSTON UNIVERSITY 13

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] Aqueous solutions at the same temperature are combined, a reaction occurs, and the temperature of the combined solutions goes up. The **water** is ...

13% 1. the system  
 80% 2. the surroundings  
 7% 3. neither system nor surroundings

BOSTON UNIVERSITY 14

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] Aqueous solutions at the same temperature are combined, a reaction occurs, and the temperature of the combined solutions goes up. The **reactants** are ...

18% 1. the system  
 0% 2. the surroundings  
 82% 3. part of the system  
 0% 4. part of the surroundings

BOSTON UNIVERSITY 15

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] Aqueous solutions at the same temperature are combined, a reaction occurs, and the temperature of the combined solutions goes up. The **reactants and products** together are ...

94% 1. the system  
 0% 2. the surroundings  
 0% 3. part of the system  
 6% 4. part of the surroundings

BOSTON UNIVERSITY 16

Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

[Quiz] Acetic acid dissolves in water as a weak electrolyte,  
 $\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$   
 In the acetic acid solution, the acetate ion,  $\text{CH}_3\text{COO}^-(aq)$ , is ...

- 0% 1. the system  
 0% 2. the surroundings  
 100% 3. part of the system  
 0% 4. part of the surroundings



17

Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

Heat depends on whether there is work

 $\Delta U = q_v$  can be different from  $\Delta H = q_p$ 

$$\Delta U = q + w = q_v + 0 \quad \Delta H \equiv q_p$$

If we prevent any volume change, then  $w = -P_{\text{ext}} \Delta V = 0$



H = enthalpy



18

Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

Heat depends on whether there is work  $q_p \neq q_v$

For a given chemical transformation of given amount of material, the energy change is fixed,

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

$$\Delta U = \frac{P}{R} \Delta V = \frac{U_{\text{final}}}{U_{\text{initial}}}$$

If the process takes place in a **sealed, rigid container**, there can be **no volume change** and so **work is 0**,

$$w = -P \Delta V = -P_{\text{ext}} \times 0 = 0$$

This means **all of the energy change** must appear as **heat**.



19

Lecture 9 CH131 Summer 1 2019

Copyright © 2019 Dan Dill dan@bu.edu

Heat depends on whether there is work

For a given chemical transformation of given amount of material, the energy change is fixed,

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

If the process takes place in an **open container**, there may be **volume change** (if there is net formation or consumption of gas) and so work may **not be 0**,

$$w = -P \Delta V \neq 0$$

This means **only some of the energy change** appears as **heat**.



20

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

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

BOSTON UNIVERSITY

21

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] Without having measured the reaction

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

if it were carried out in an **open** beaker we know that ...

100% 1. work is done on the surroundings,  $w < 0$ .  
 0% 2. work is done on the system,  $w > 0$ .  
 0% 3. no work is done.  
 0% 4. Unable to say without further information

BOSTON UNIVERSITY

22

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] Without having measured the reaction

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

if it were carried out in a **sealed** beaker we know that ...

0% 1. work is done on the surroundings,  $w < 0$ .  
 6% 2. work is done on the system,  $w > 0$ .  
 94% 3. no work is done.  
 0% 4. Unable to say without further information

BOSTON UNIVERSITY

23

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP]  $\text{NaHCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CO}_2(g) + \text{Na}^+(aq) + 2 \text{H}_2\text{O}(l)$  is **endothermic**,  $q > 0$  (solution/surroundings cool). How much cooling is there at **constant volume** ( $q_v$ ), compared to that at constant pressure ( $q_p$ )?

13% 1. Cooling is **smaller** at constant volume,  $q_v < q_p$   
 0% 2. Cooling is **the same** at constant volume,  $q_v = q_p$   
 88% 3. Cooling is **greater** at constant volume,  $q_v > q_p$   
 0% 4. Unable to know without further information

BOSTON UNIVERSITY

24

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

### $\Delta U = q_V$ versus $\Delta H = q_P$

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

BOSTON UNIVERSITY

25

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

**[Quiz]** 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). How much warming is there at constant volume ( $q_V$ ), compared to that at constant pressure ( $q_P$ )?

- 41% 1. Warming is greater at constant volume,  $|q_V| > |q_P|$
- 0% 2. Warming is the same at constant volume,  $|q_V| = |q_P|$
- 59% 3. Warming is smaller at constant volume,  $|q_V| < |q_P|$
- 0% 4. Unable to know without further information

BOSTON UNIVERSITY

26

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

### $\Delta U = q_V$ versus $\Delta H = q_P$

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

BOSTON UNIVERSITY

27

Lecture 9 CH131 Summer 1 2019 Copyright © 2019 Dan Dill dan@bu.edu

### $q_P$ differs only a little from $q_V$

$$\Delta U = q_V = q_P + w$$

$$q_V - q_P = w = -P_{\text{ext}} \Delta V = -\Delta n_g R T$$

$$\Delta n_g = n_g(P) - n_g(R) = 1 \text{ mol} - 3 \text{ mol} = -2 \text{ mol}$$

For 1 mol change in the amount of gas as a result of the reaction:

$$1 \text{ mol} \times RT = 8.314 \text{ J/K} \times 300 \text{ K} \approx 2.5 \text{ kJ}$$

Typical values of  $q$  are several orders of magnitude larger, and so  $q_V$  and  $q_P$  always have the same sign.

$w_{\text{ext}} \sim 2.5$   
 $q_{V, \text{ext}} \sim 100$

BOSTON UNIVERSITY

28