[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 ...
$\left(R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}\right)$

0% 1. 250 g/mol
0% 2. 500 g/mol
0% 3. 1000 g/mol
11% 4. 2500 g/mol
0% 5. 5000 g/mol
11% 6. Some other value
78% 7. Not sure

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Lecture 10 CH131 Summer 1 2021

Thursday, June 10, 2021

- Complete: Osmotic pressure, $\Pi = RTM_c$;

Ch12: Thermodynamic processes and thermochemistry

- First law of thermodynamics: $\Delta U = q + w$
- Measuring heat and measuring work
- Heat, q, depends on whether $w \neq 0$: $\Delta U = q_V$ and $\Delta H = q_P$
- Enthalpy change of reaction, $\Delta H°_{rxn}$
- Enthalpy changes are additive: Hess's law

Next: Practice problem: Limiting reagent, Δn_{gas}, w_{PV}, q_P, q_V; Standard enthalpy of formation, $\Delta H°_f$; Using $\Delta H°_f$ to compute $\Delta H°_{rxn}$; Begin ch13: Spontaneous Processes

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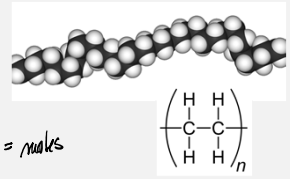
Osmotic pressure $\Pi = i\, c_{solute} R\, T$

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. $\left(R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}\right)$



1. C: Calculate the concentration...
   1.00×10^{-4} mol/L = C_{solute}
2. M: Calculate the moles...
   10^{-5} mol
   $C_{solute} \times V$ = moles
3. W: Calculate the molecular weight ...
   $1.40 \times 10^{+5}$ g/mol
   1.40 g / moles

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[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 ...
$\left(R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}\right)$

1.0×10^{-3} L

C: $C_{solute} = \Pi / RT = \frac{1.0 \times 10^3 \text{ Pa}}{R * 298\text{K}}$

M: moles = $C_{solute} *$ volume

W = mass / moles = 1.0×10^{-3} g.

0% 1. 250 g/mol
0% 2. 500 g/mol
0% 3. 1000 g/mol
100% 4. 2500 g/mol
0% 5. 5000 g/mol
0% 6. Some other value
0% 7. Not sure

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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

How do we know heat is present?

Heat flow is measured indirectly by temperature change in the surroundings.

The temperature of the chemical system (reactants and products) does not change, only the temperature of the surroundings.

How do we know heat is present?

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

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

How do we know heat is present?

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

energy flow into system from surroundings ...

energy of system goes up ...

and so, $q > 0$.

How do we know heat is present?

If $q > 0$ the process is called endothermic.

The system gains energy in the form of heat from the surroundings.

The surroundings cools, $\Delta T_{sur} < 0$.

There is no change in the temperature of the system, $\Delta T_{sys} = 0$, since all of the energy is used in the net breaking of chemical bonds, rather than to increase motion of the particles of the system.

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How do we know heat is present?

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

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How do we know heat is present?

If $q < 0$ the process is called exothermic.

The system loses energy in the form of heat to the surroundings.

The surroundings warms, $\Delta T_{sur} > 0$.

There is no change in the temperature of the system, $\Delta T_{sys} = 0$, since all of the energy comes from net making of chemical bonds, rather than the slowed motion of the particles of the system.

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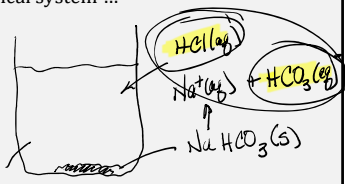
[TP] When $NaHCO_3(s)$ is dissolved in 200 mL of $HCl(aq)$, the temperature of the solution goes down. This means the chemical reaction between the $NaHCO_3(s)$ and the $HCl(aq)$ results in the chemical system ...

0%	1.	giving off heat and so $q > 0$
0%	2.	giving off heat and so $q < 0$
0%	3.	absorbing heat and so $q < 0$
100%	4.	absorbing heat and so $q > 0$
0%	5.	Not sure



$\Delta T_{sur} = \Delta T_{solution} < 0$

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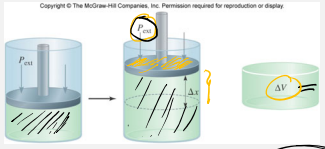
How do we know if work is present?

Macroscopic movement, for example of a piston.



Work done by gas: force × distance $= \frac{F_{ext}}{A} \times \Delta x \, A = P_{ext} \Delta V$

Work done on gas: $w = -P_{ext} \Delta V = \cdots$

$= A P_{ext} \, distance = P_{ext} \Delta V$

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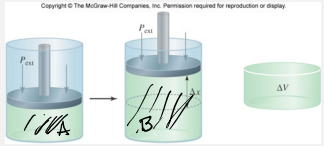
How do we know if work is present?

Macroscopic movement, for example of a piston.



Work done on gas: $w = -P_{ext} \Delta V = -\Delta n_{gas} RT$

Expansion of gas pushes against P_{ext}: gas expends energy, $w < 0$

Compression of gas pushed on by P_{ext}: gas gains energy, $w > 0$

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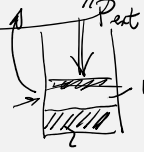
[TP] When $NaHCO_3(s)$ is dissolved in 200 mL of $HCl(aq)$, $CO_2(g)$ bubbles form. This means the chemical reaction between the $NaHCO_3(s)$ and the $HCl(aq)$ results in the chemical system ...

0%	1.	doing work and so $w > 0$
77%	2.	doing work and so $w < 0$
0%	3.	having work done on it and so $w > 0$
0%	4.	having work done on it and so $w < 0$
23%	5.	Not sure



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Heat depends on whether there is work

Energy change in chemical reactions is due to the balance of the energy required to break bonds and the energy released when bonds are made.

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Heat depends on whether there is work

No matter how the chemical reaction is carried out (in a sealed, constant volume container or in an open, constant-pressure container), for a given amount of reactants and a given reaction yield, the energy change,

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

is fixed, by the number and kinds of bonds being made and broken.

Heat depends on whether there is work

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

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

$\Delta U = q_V$.

This means all the energy change must appear as heat flow between the system and the surroundings.

Heat depends on whether there is work

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,

$w = -P_{\text{ext}}\,\Delta V \neq 0$

This means only some of the energy change must appear as heat flow, the remainder being account for as work.

rigid, sealed container: $\Delta U = q_V$

open container: $\Delta U = q_P + w_{PV}$

Energy diagrams relate $\Delta U = q_V$ and $\Delta H = q_P$

$\Delta V > 0$, $w_{PV} < 0$

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

[TP] The combustion $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ 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)?

8% 1. Warming is greater at constant volume, $|q_V| > |q_P|$
0% 2. Warming is the same at constant volume, $|q_V| = |q_P|$
92% 3. Warming is smaller at constant volume, $|q_V| < |q_P|$
0% 4. Unable to know without further information
0% 5. Not sure

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Energy diagrams relate $\Delta U = q_V$ and $\Delta H = q_P$

The combustion $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ 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)?

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$\Delta H \equiv q_P$ differs only a little from $\Delta U \equiv q_V$

Energy change: $\Delta U = q_V = q_P + w$

Enthalpy change: $\Delta H \equiv q_P$

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

For 1.0 mol change in the amount of gas as a result of the reaction,

$1.0\ \text{mol} \times RT = 1.0\ \text{mol} \times 8.314\ \text{J/(mol K)} \times 300\ \text{K} \approx 2.5\ \text{kJ}$

so $\Delta U = q_V$ and $\Delta H \equiv q_P$ differ little from one another.

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

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$\Delta H = q_P$ differs only a little from $\Delta U = q_V$

Energy change: $\Delta U = q_V = q_P + w$

Enthalpy change: $\Delta H \equiv q_P$

In the open laboratory (constant pressure), pressure is constant, so it is convenient to work with enthalpy change.

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Enthalpy change of reaction, $\Delta H°_{rxn}$

We have seen that while heat flow at constant volume is the direct measure of energy change ($\Delta U = q_V$), heat flow at constant pressure (q_P) is much more convenient to measure and differs only a little bit from q_V.

For this reason from now on we will focus on enthalpy change, $\Delta H = q_P$.

Enthalpy change of reaction, $\Delta H°_{rxn}$

How much heat flows depends on how much limiting regent there is and on the yield of the chemical reaction.

To standardize the reporting of enthalpy changes, the standard enthalpy change of reaction ($\Delta H°_{rxn}$) is defined as the heat flow at SATP (1 bar and 25°C) for the chemical equation as written.

Enthalpy change of reaction, $\Delta H°_{rxn}$

Consider the chemical equation

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g) \quad \Delta H°_{rxn} = -114.1\ \frac{kJ}{mol}$$

Here are the different ways to use this chemical equation and its enthalpy change value.

"114.1 kJ of heat are released for each 2 mol of $NO_2(g)$ formed."

"114.1 kJ of heat are released for each 2 mol of $NO(g)$ consumed."

"114.1 kJ of heat are released for each 1 mol of $O_2(g)$ consumed."

"114.1 kJ of heat are released for each reaction unit."

"114.1 kJ of heat are released for each mol of reaction."

Enthalpy change of reaction, ΔH

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g) \quad \Delta H°_{rxn} = -114.1\ \frac{kJ}{mol}$$

If 11.5 g $NO(g)$ reacts completely with excess oxygen, what is q_P?

$$q_P = 11.5\ g\ \frac{mol\ NO}{30.0\ g} \times \frac{mol\ rxn}{2\ mol\ NO} \times \frac{-114.1\ kJ}{mol\ rxn} = -21.9\ kJ$$

[TP] The enthalpy change of reaction for

$2\,A + 3\,B \rightarrow 4\,C + D$

is $\Delta H°_{rxn} = -45\ \frac{kJ}{mol}$. If 2.0 mol of A reacts with 2.0 mol of B with 50.% yield, then the heat flow at constant pressure for the process is ...

0% 1. $q_P = -90.\ kJ$
0% 2. $q_P = -45.\ kJ$
0% 3. $q_P = -30.\ kJ$
100% 4. $q_P = -15.\ kJ$
0% 5. something else
0% 6. Not sure

Rules for Hess's law calculations

Adding reactions, their heat flow adds.

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Each multiple of a reaction adds a multiple to its heat flow to the total.

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Each multiple of a reaction adds a multiple to its heat flow to the total.

Exchanging reactants and products reverses the direction of the heat flow.

Rules for Hess's law calculations

Adding reactions, their heat flow adds.

Each multiple of a reaction adds to its heat flow to the total.

Exchanging reactants and products reverses the direction of the heat flow.

Operation	Result
Addition of two or more chemical equations	$\Delta H^\circ_{rxn}(1+2) = \Delta H^\circ_{rxn}(1) + \Delta H^\circ_{rxn}(2)$
Multiplication of a chemical equation by a factor of n	$\Delta H^\circ_{rxn} = n\Delta H^\circ_{rxn}(1)$
Reversing a chemical equation	$\Delta H^\circ_{rxn}(\text{reverse}) = -\Delta H^\circ_{rxn}(\text{forward})$

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ΔH°_{rxn} via Hess's law

Use energy conservation to determine ΔH of the third reaction below.

A ⟶ B	ΔH_1
C ⟶ B	ΔH_2
A ⟶ C	ΔH_3 = ?

Since energy is conserved ...

$\Delta H_3 = \Delta H_1 - \Delta H_2$

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ΔH°_{rxn} via Hess's law

Use energy conservation to determine ΔH of the third reaction below.

A ⟶ B	$\Delta H_1 = +85$ kJ
C ⟶ B	$\Delta H_2 = -52$ kJ
A ⟶ C	ΔH_3 = ?

Since energy is conserved ...

$\Delta H_3 = (\Delta H_1 - \Delta H_2) = (+85 \text{ kJ} - (-52 \text{ kJ})) = +137$ kJ

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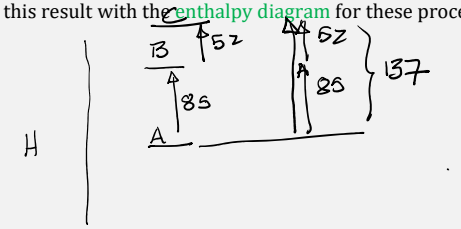
ΔH°_{rxn} via Hess's law

A ⟶ B	$\Delta H_1 = +85$ kJ
C ⟶ B	$\Delta H_2 = -52$ kJ
A ⟶ C	$\Delta H_3 = \Delta H_1 - \Delta H_2 = +85 \text{ kJ} - (-52 \text{ kJ}) = +137$ kJ

Illustrate this result with the enthalpy diagram for these processes.



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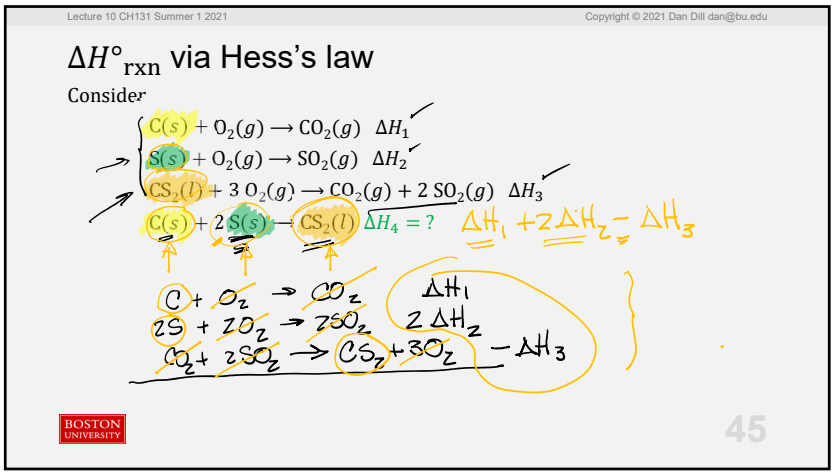
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ΔH°rxn via Hess's law
Consider
C(s) + O2(g) → CO2(g) ΔH1
S(s) + O2(g) → SO2(g) ΔH2
CS2(l) + 3 O2(g) → CO2(g) + 2 SO2(g) ΔH3
C(s) + 2 S(s) → CS2(l) ΔH4 = ?
ΔH1 + 2ΔH2 − ΔH3
C + O2 → CO2
2S + 2O2 → 2SO2
CO2 + 2SO2 → CS2 + 3O2
ΔH1
2 ΔH2
−ΔH3
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