Lecture 10 CH131 Summer 1
Wednesday, June 10, 2020

- System and surrounding
- Heat depends on whether there is work
- Enthalpy change of reaction, $\Delta_r H$
- Hess's law

Next lecture: Standard enthalpy of formation of X, $\Delta_f H°(X)$; Example thermochemistry problems; Begin Ch13: Spontaneous Processes

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Sign conventions for *q* and *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

Direction of Energy Transfer	Sign Convention	Effect on U_{system}
Heat flow from surroundings to system	$q > 0$ (+)	U increases, $\Delta U > 0$
Heat flow from system to 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, $\Delta U < 0$

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

67% 1. the system
27% 2. the surroundings
7% 3. neither system nor surroundings

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0

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

50% 1. the system
13% 2. the surroundings
38% 3. part of the system
0% 4. part of the surroundings

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0

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[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 ...

80% 1. the system
0% 2. the surroundings
20% 3. part of the system
0% 4. part of the surroundings

system has lost energy
solutions (surroundings) gain energy
$q < 0$

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[TP] Acetic acid dissolves in water as a weak electrolyte,

$$CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$$

In the acetic acid solution, the acetate ion, $CH_3COO^-(aq)$, is ...

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

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ΔH enthalpy

Heat depends on whether there is work

$\Delta U = q_V$ can be different from $\Delta H = q_P$

$mC\Delta T$

① $\Delta U = q + w$
② If $\Delta V = 0$, $w = 0$
③ Therefore, if we keep volume constant, $w = 0$ and $q = q_V$

$\Delta U = q_V$ $q = q_{sys} = -q_{surr}$

$q_{surr} = mass_{surr} * heat\ capacity * \Delta T_{surr}$

heat capacity
$\frac{J}{g\,K}$ specific heat
$\frac{J}{mol\,K}$ heat capacity

Heat depends on whether there is work

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

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

$A(s) \rightarrow B(g)$ $\Delta U = -20\,kJ$

A

$-20\,kJ$

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

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

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

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.

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Heat depends on whether there is work

The reaction

$NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\,H_2O(l)$

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)?

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[TP] Without having measured the reaction

$NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\,H_2O(l)$

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

65% 1. work is done on the surroundings, $w < 0$.
35% 2. work is done on the system, $w > 0$.
0% 3. no work is done.
0% 4. Unable to say without further information

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[TP] Without having measured the reaction

$NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\,H_2O(l)$

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

13% 1. work is done on the surroundings, $w < 0$.
31% 2. work is done on the system, $w > 0$.
56% 3. no work is done.
0% 4. Unable to say without further information

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[TP] $NaHCO_3(s) + H_3O^+(aq) \rightarrow CO_2(g) + Na^+(aq) + 2\ H_2O(l)$ 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)?

6% 1. Cooling is smaller at constant volume, $q_V < q_P$
38% 2. Cooling is the same at constant volume, $q_V = q_P$
56% 3. Cooling is greater at constant volume, $q_V > q_P$
0% 4. Unable to know without further information

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

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

[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)?

39% 1. Warming is greater at constant volume, $|q_V| > |q_P|$
6% 2. Warming is the same at constant volume, $|q_V| = |q_P|$
56% 3. Warming is smaller at constant volume, $|q_V| < |q_P|$
0% 4. Unable to know without further information

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

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

q_P differs only a little from q_V

$\Delta U = q_V = q_P + w$

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

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.

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Enthalpy change of reaction, $\Delta_r H$ =

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Enthalpy change of reaction, $\Delta_r H$

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g) \quad \Delta_r H = -114.1\ \text{kJ}$

"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 consumed."

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

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

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Enthalpy change of reaction, $\Delta_r H$

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g) \quad \Delta_r H = -114.1\ \text{kJ}$

If 2.90 mol $NO(g)$ react completely with excess oxygen, what is q_P?

$q_P = 2.90\ \text{mol NO} \times -114.1\ \text{kJ/(2 mol NO)}$

$= -165\ \text{kJ}$

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

$q_P = 11.5\ \text{g} \times\ \text{mol NO/(30.0 g)} \times -114.1\ \text{kJ/(2 mol NO)}$

$= -21.8\ \text{kJ}$

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[TP] The enthalpy change of reaction for

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

is $\Delta_r H = -45$ kJ. If 1 mol of A reacts with 1 mol of B with 100 % yield, then q_P for the process is ...

0% 1. −90 kJ
6% 2. −45 kJ
6% 3. −30 kJ
89% 4. −15 kJ
0% 5. Further information required

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$\Delta_r H°$ via Hess's law

Consider

$A \rightarrow B \quad \Delta_r H°_1$

$C \rightarrow B \quad \Delta_r H°_2$

$A \rightarrow C \quad \Delta_r H°_3 = ?$

Since energy is conserved ...

$$\Delta_r H°_3 = \Delta_r H°_1 - \Delta_r H°_2$$

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$\Delta_r H°$ via Hess's law

Consider

$A \rightarrow B \quad \Delta_r H°_1 = +85$ kJ

$C \rightarrow B \quad \Delta_r H°_2 = -52$ kJ

$A \rightarrow C \quad \Delta_r H°_3 = ?$

Since energy is conserved ...

$$\Delta_r H°_3 = \Delta_r H°_1 - \Delta_r H°_2 = +85\ \text{kJ} - (-52\ \text{kJ}) = +137\ \text{kJ}$$

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$\Delta_r H°$ via Hess's law

Consider

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H°_1$

$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_r H°_2$

$CS_2(l) + 3\ O_2(g) \rightarrow CO_2(g) + 2\ SO_2(g) \quad \Delta_r H°_3$

$C(s) + 2\ S(s) \rightarrow CS_2(l) \quad \Delta_r H°_4 = ?$

Since energy is conserved ...

$$\Delta_r H°_4 = \Delta_r H°_1 + 2\ \Delta_r H°_2 - \Delta_r H°_3$$

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$\Delta_r H^\circ$ via Hess's law

Consider

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H^\circ_1 = -393.5$ kJ

$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_r H^\circ_2 = -296.8$ kJ

$CS_2(l) + 3\,O_2(g) \rightarrow CO_2(g) + 2\,SO_2(g) \quad \Delta_r H^\circ_3 = -1103.9$ kJ

$C(s) + 2\,S(s) \rightarrow CS_2(l) \quad \Delta_r H^\circ_4 = ?$

Since energy is conserved ...

$\Delta_r H^\circ_4 = \Delta_r H^\circ_1 + 2\,\Delta_r H^\circ_2 - \Delta_r H^\circ_3 = +116.8$ kJ

$= -393.5 + 2(-296.8) - (-1103.9)$

Calculation of q_V and q_P

$2\,Al(s) + 6\,HCl(aq) \rightarrow 2\,AlCl_3(aq) + 3\,H_2(g) \quad \Delta_r H^\circ_1 = -1049$ kJ

$HCl(g) \rightarrow HCl(aq) \quad \Delta_r H^\circ_2 = -79$ kJ

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g) \quad \Delta_r H^\circ_3 = -185$ kJ

$AlCl_3(s) \rightarrow AlCl_3(aq) \quad \Delta_r H^\circ_4 = -323$ kJ

(a) Calculate $\Delta_r H^\circ$ for the reaction

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$

$\Delta H_1 + 6\Delta H_2 + 3\Delta H_3 - 2\Delta H_4$

Calculation of q_V and q_P

$2\,Al(s) + 6\,HCl(aq) \rightarrow 2\,AlCl_3(aq) + 3\,H_2(g) \quad \Delta_r H^\circ_1 = -1049$ kJ

$HCl(g) \rightarrow HCl(aq) \quad \Delta_r H^\circ_2 = -79$ kJ

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g) \quad \Delta_r H^\circ_3 = -185$ kJ

$AlCl_3(s) \rightarrow AlCl_3(aq) \quad \Delta_r H^\circ_4 = -323$ kJ

(a) Calculate $\Delta_r H^\circ$ for the reaction

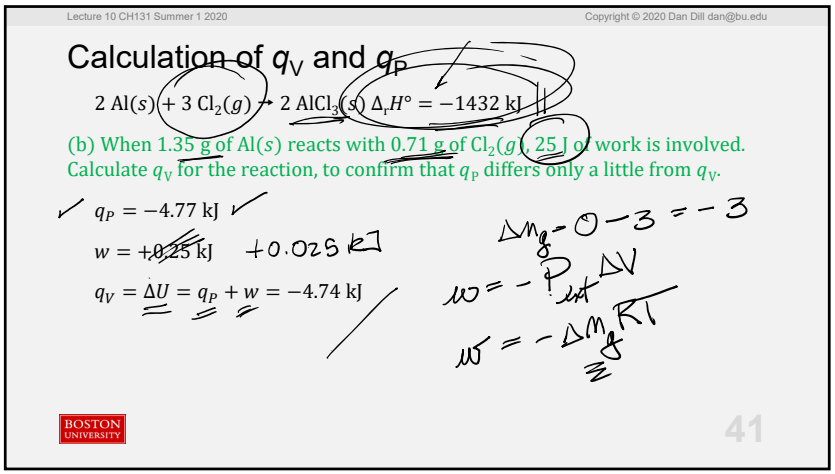
$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$

$\Delta_r H^\circ = \Delta_1 H^\circ + 6\Delta_2 H^\circ + 3\Delta_3 H^\circ - 2\Delta_4 H^\circ = -1432$ kJ

Calculation of q_V and q_P

$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s) \quad \Delta_r H^\circ = -1432$ kJ

(b) When 1.35 g of $Al(s)$ reacts with 0.71 g of $Cl_2(g)$, 25 J of work is involved. Calculate q_V for the reaction, to confirm that q_P differs only a little from q_V.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Calculation of q_V and q_P
$2\ Al(s) + 3\ Cl_2(g) \rightarrow 2\ AlCl_3(s)\ \Delta_r H° = -1432\ kJ$
(b) When 1.35 g of $Al(s)$ reacts with 0.71 g of $Cl_2(g)$, 25 J of work is involved. Calculate q_V for the reaction, to confirm that q_P differs only a little from q_V.
$q_P = -4.77\ kJ$
$w = +0.25\ kJ$
$+0.025\ kJ$
$q_V = \Delta U = q_P + w = -4.74\ kJ$
$\Delta n_g = 0 - 3 = -3$
$w = -P\Delta V$
$w = -\Delta n_g RT$
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