



MEGA LECTURE

Chapter

7

THERMOCHEMISTRY

MATHEMATICAL EQUATIONS

Units of energy

The SI unit of heat energy is Joule (J)

$$J = Nm$$

$$N = kg\ ms^{-2}$$

So,

$$J = kg\ m^2\ s^{-2}$$

$$1000\ J = 1\ kJ$$

Energy is expressed per mole of the substance.

Hence ΔE or ΔH is given the units of $kJ\ mol^{-1}$. Specific heat has units of $J\ g^{-1}\ K^{-1}$.

Important mathematical equations

Equation for 1st law of thermodynamics

$$\Delta E = q + w$$

$$dE = dq + dw$$

where

dE = change of internal energy

dq = amount of heat absorbed

dw = amount of work done

Pressure volume work done

$$P\Delta V = W$$

$q_v = \Delta E$ = amount of heat absorbed at constant volume

$q_p = \Delta H$ = amount of heat absorbed at constant pressure

Relationship between enthalpy change and internal energy change

$$\Delta H = \Delta E + P\Delta V$$

Relationship of heat and temperature

$$Q = m \times S \times \Delta T$$

Q = amount of heat absorbed or evolved

m = mass of substance absorbing heat

S = specific heat

ΔT = change in temperature

Hess's law of heat summation

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

where

ΔH = enthalpy change in a single step of overall reaction

$\Delta H_1, \Delta H_2, \Delta H_3$ etc., are the enthalpy changes in various steps.

Born-Haber cycle

Heat of formation of an ionic compound = heat of sublimations of the metal + heat of dissociation of electronegative element + heat of ionization of the metal + electron affinity of electronegative element + lattice energy of crystalline substance.

$$\Delta H_f^\circ = \Delta H_s^\circ + \Delta H_{D2}^\circ + \Delta H_i^\circ + \Delta H_E^\circ + \Delta H_l^\circ$$

METHODS TO SOLVE THE NUMERICAL PROBLEMS

(a)

Numericals of calorimeter

Equation used

$$Q = m \times S \times \Delta T$$

m = mass of calorimeter + stirrer + water

S = specific heat of water and calorimeter

ΔT = rise or fall of temperature

While doing the calculations from bomb calorimeter, the specific heat is taken in $K^{-1} mol^{-1}$.

(b)

Numericals of Hess's law

Hess's law is mostly used for the calculation of enthalpy for those chemical reactions whose enthalpy changes cannot be measured directly.

We are given two types of equations:

- (1) Those equations whose enthalpy changes are given. These equations are written in the balanced form along with ΔH values and the phases of the substances, because these are thermochemical equations.
- (2) That equation whose enthalpy change is to be calculated, is also written in a balanced form. In most of the cases, we have to construct this equation ourselves.

The given equations are multiplied with certain digits (if required), added and sometimes subtracted from others to get the required equation.

DEFINITIONS

(May be used in short questions with examples)

(1) **Adiabatic process:**

That process in which no exchange of heat takes place between the system and surrounding. In other words $\Delta q = 0$.

(2) **Born-Haber cycle:**

(Rwp. 2014)

According to this cycle, the energy change in a cyclic process is always equal to zero. It is mostly used for theoretical calculations of lattice energy of a crystal. This cycle is another shape of first law of thermodynamics.

(3) **Closed system:**

That system in which mass cannot cross the boundaries of the system and surrounding, but energy can cross. A closed vessel having a hot water cools down when placed in air. Heat can exchange with surrounding but mass does not.

(4) **Endothermic reactions:** (Lahore 2011, D.G. Khan 2012, M. Pure 2012, D.G. Khan 2013)

Those chemical reactions which take place with the absorption of heat. The energy of the products is greater than the energy of the reactants. The dissociation of H_2 into H-atoms absorbs 436 kJ mol^{-1} of energy.

(5) **Enthalpy:** (Multan 2012, R. Pindi 2012)

It is the total heat content of the system and is denoted by H. The change of enthalpy is measured at constant pressure. The change of enthalpy is denoted by ΔH .

(6) **Exothermic reactions:** (Lahore 2011, D.G. Khan 2012, M. Pure 2012, D.G. Khan 2013)

Those chemical reactions which take place with the evolution of heat are called exothermic reactions. The energy of the products is less than the those of reactants. The formation of H_2O from H_2 and O_2 gives $285.5 \text{ kJ mol}^{-1}$ of energy.

(7) **Final state of system:**

It is the description of the system after it has undergone a change.

(8) **First law of thermochemistry:**

The amount of heat which is required to decompose a compound into its elements is equal to the amount of heat which is evolved during the formation of that compound from its elements. Dissociation of 1 mole of H_2 into 2H requires 436 kJ of energy and same is evolved when 2 moles of H combine to give 1 mole of H_2 .

(9) **First law of thermodynamics:** (Rwp. 2014, Multan 2014)

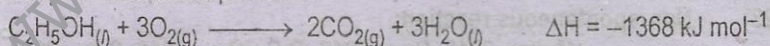
It is stated in three ways:

- (i) Energy can neither be created nor destroyed although it may change from one form to the other.
- (ii) The total energy of the system and the surrounding is always constant.
- (iii) The energy of the universe remains constant.

Mathematically $q = W + \Delta E$

(10) **Heat of combustion:** (Sargodha 2008, Multan 2011, F. Abad 2014, Guj. 2014)

It is amount of heat which is evolved when one mole of a substance is completely oxidized. It is mostly an exothermic process.

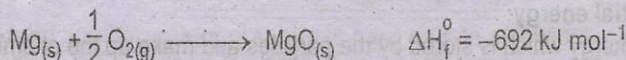


(11) **Heat of dilution:**

It is change in enthalpy, when one mole of the substance is diluted to such an extent, that no heat is evolved or absorbed on further dilution.

(12) **Heat of formation:** (Lahore 2012)

It is the amount of heat which is evolved or absorbed, when one mole of a substance is formed from its constituent elements under the given conditions of temperature and pressure.



(13) **Heat of hydration:**

It is the amount of heat which is evolved or absorbed when one mole of any anhydrous salt combines with required number of moles of water to form a specific hydrate.

(14) Heat of neutralization: (Mirpur-2006, Sargodha 2010, Multan 2013, Lahore 2014)

It is the amount of heat which is evolved or absorbed, when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base in dilute solution. Its value for a strong acid and a strong base is -57 kJ mol^{-1} .

(15) Heat of solution:

It is the amount of heat which is evolved or absorbed when one mole of a solute is dissolved completely in large excess of water, so that further dilution of a solution does not produce any heat change.

The heat of solution of NH_4Cl is $+16.2 \text{ kJ mol}^{-1}$ and that of Na_2CO_3 is -25 kJ mol^{-1} .

(16) Hess's law of heat summation: (Lahore 2012, Rwp. 2014)

According to this law, the amount of heat change (ΔH or ΔE) in a chemical reaction remains the same whether the reaction completes in one step or in more than one steps. You can prepare CO_2 in a single step or two steps. The heat of formation is $-393.7 \text{ kJ mol}^{-1}$.

(17) Initial state of system:

It is the description of the system before it undergoes any change.

(18) Internal energy change: (Gujranwala-2006)

It is the amount of heat evolved or absorbed by the system at constant volume.

(19) Internal energy of chemical system: (Gujranwala-2006, R. Pindi 2012, Lahore 2014)

It is the sum total of kinetic and potential energies of all the particles, which make up the chemical system. For a molecule it is the sum of rotational, vibrational and translational motions.

(20) Isolated system:

That system which neither exchanges the energy nor matter with its surroundings is called isolated system. Let tea in a thermos is an isolated system.

(21) Isothermal processes:

That process which takes place at constant temperature is called isothermal process.

(22) Joule:

It is the unit of energy, and it is expended when a force of one Newton acts over a distance of one meter. $J = \text{Nm}$ since $N = \text{kg ms}^{-2}$ $\therefore J = \text{kg m}^2 \text{s}^{-2}$. It is smaller than calorie, since $1 \text{ cal} = 4.185$.

(23) Non-spontaneous reaction:

(Multan 2012, Rwp. 2013, D.G. Khan 2013, Sarg. 2014, F. Abad 2014)

Those chemical reactions which do not happen of their own and only an external agency is required to do such reactions. The decomposition of H_2O to give H_2 and O_2 requires electrical current.

(24) Open system:

That system in which both matter and energy can exchange with its surrounding. A boiling water in open vessel in open system.

(25) Potential energy:

That energy which is stored by the particles and make up the chemical system due to position, condition or composition of the system.

(26) Specific heat:

It is the amount of heat which is required to raise the temperature of one gram of a substance by one Kelvin. Its units are $\text{J g}^{-1} \text{K}^{-1}$. Sometimes it is expressed as $\text{J mol}^{-1} \text{K}^{-1}$.

(27) Spontaneous reactions:

(Multan 2012, Rwp. 2013, D.G. Khan 2013, Sarg. 2014, F. Abad 2014)

Those chemical reactions which happen of their own without the help of an external agency. The burning of carbon to give CO_2 is a spontaneous process.

(28) Standard enthalpy change:

It is the enthalpy change when the reactants and products of the reaction are in their standard state. It is represented by ΔH° . The ΔH° value for CO_2 formation from C and O_2 is $-393.7 \text{ kJ mol}^{-1}$.

(29) Standard state of a substance:

It is the physical state of a pure substance at one atmospheric pressure and 25°C .

(30) State function: (Multan 2007, Sarg. 2011, Lahore 2014, B. Pur 2014, Multan 2014)

That property which depends only on the state of a system is called state function.

ΔH , ΔE , ΔG are state functions. Their values do not depend upon the route.

(31) State of a system:

The conditions of a system described by a set of variables as pressure, temperature, volume and number of moles is called state of a system.

(32) Surrounding: (Guj. 2008, Faisalabad 2010, Lahore, 2011, D.G. Khan, 2011, D.G. Khan 2012, F. Abad 2012, Rwp. 2013, Lahore 2014, Sahiwal 2014)

The environment containing the system is called surrounding. The air surrounding a hot cup of tea is surrounding of the cup.

(33) System: (Multan 2007, Guj. 2008, Faisalabad 2010, Lahore 2011, D.G. Khan 2011, F. Abad 2012, D.G. Khan 2012, Rwp. 2013, Lahore 2014, B. Pur 2014, Sahiwal 2014)

A material or a collection of materials, which is under study is called a system. The hot tea in a cup is a system.

(34) Thermochemical reactions: (Lahore 2012, Lahore 2014)

Those chemical reactions, which happen with the evolution or absorption of heat.

(35) Thermochemistry:

It is that branch of chemistry which deals with the heat energy changes along with the phase changes and occurring of the chemical reactions.

(36) Thermodynamics:

That branch of science which deals with the energy changes of physical and chemical processes. It also deals with the transformation of one form of energy into the other. It gives us the information about the feasibility of process. This feasibility is decided by the free energy change.

MULTIPLE CHOICE QUESTIONS (EXERCISE OF THE TEXTBOOK)

MULTIPLE CHOICE QUESTIONS	ANSWER WITH REASONS
(1) If an endothermic reaction is allowed to take place very rapidly in the air, the temperature of the surrounding air: (a) remains constant (b) increases (c) decreases (d) remain unchanged	1. (c) (Rawalpindi Board 2005, Lahore 2012, F. Abad 2014) In endothermic reactions heat is absorbed. This heat is taken by the system from the surrounding, hence the temperature of the surrounding air falls.
(2) In endothermic reactions, the heat content of the: (a) products is more than that of reactants	2. (a) Endothermic reactions happen with the absorption of heat. When the reaction is endothermic, it absorbs the heat. It means that the heat content of the products

ANSWERS TO THE SHORT QUESTIONS

General Features Of Thermochemistry

Q.1 How the temperature of the system changes during exothermic and endothermic reactions?

-1 حرارت خارج کرنے والے اور جذب کرنے تعاملات سسٹم کے درجہ حرارت کو کیسے تبدیل کرتے ہیں؟

Ans: In an exothermic reaction (حرارت باہر نکلنے والے), heat is evolved which increases the temperature of the system. In an endothermic reaction (حرارت جذب کرنے والے), heat is absorbed, so the temperature of the system falls down. These statements are true when the system is isolated (الگ تھلگ ہو).

Q.2 What is a spontaneous and a non-spontaneous process?

(Federal-2006, Rwp. 2008, F. Abad 2008, Lahore 2009, Multan 2009, Guj. 2010, Rwp 2011, Faisalabad 2011, Multan 2011, Guj. 2012, D.G. Khan 2014, D.G. Khan 2014, Guj. 2014)

-2 خود بخود ہونے والے عمل سے کیا مراد ہے؟

Ans: That process which takes place on its own (اپنے آپ) is called spontaneous process. No external assistance (باہر کی مدد) is required. It moves from non-equilibrium (بغیر توازن والی حالت) state towards the equilibrium state. It is unidirectional (یک سمتی) and irreversible. A non-spontaneous process needs an external help to take place.

Q.3 What is state and state function?

(Multan-2006, Lahore 2008, Sarg. 2009, Lahore 2010, Sarg. 2011, Multan 2012, B. Pure 2012, Lahore 2013, Guj. 2013)

-3 سٹیٹ اور سٹیٹ فنکشن سے کیا مراد ہے؟

Ans: The condition of a system is called the state of a system. The initial state is a description (بیان) before a change happens. Final state is a description after a change takes place. State function is the macroscopic property (بغیر خوردبین کے نظر آنے والی) of a system, which has some definite values for initial and final states and is independent of the path (راستہ سے آزاد) which is adopted (اختیار کرنا) to bring out the change.

Q.4 Define ΔH_r^0 (enthalpy of reaction). Can it be negative? How?

(Gujranwala Board 2005, D.G. Khan-2006, Multan 2008, Lahore 2012, Lahore 2013, Federal 2013)

-4 کسی تعامل کی انتھالپی کی تبدیلی کی تعریف کریں۔ کیا یہ منفی بھی ہو سکتی ہے؟

Ans: ΔH_r^0 is the enthalpy change under standard conditions when the reactants are converted into products. It can be negative, if the enthalpy of the products is less than the enthalpy of the reactants. This can be assessed (اندازہ لگانا) by studying the nature of bonds (بانڈز کی نیچر) which are being broken (جو ٹوٹ رہے ہیں) and those which are being formed (جو بن رہے ہیں).

Q.5 Define the following terms: (a) Enthalpy (b) Endothermic reaction.

(Multan Board 2005, Lahore 2013)

-5 مندرجہ ذیل کی تعریف کریں۔ (a) انتھالپی (b) حرارت کو جذب کرنے والے تعامل

Ans: Enthalpy is the total heat content (جو حرارت کی کل مقدار ہے) of the system. It cannot be measured. We can only measure the enthalpy change of a system. Those

chemical reactions whose enthalpy change is positive and they absorb the heat during the progress of the reaction are called endothermic reactions.

Q.6 What is the physical significance of equation, $\Delta H = q_p$?

(D.G. Khan 2012, Federal 2013)

$\Delta H = q_p$ ایک اہم مساوات ہے۔ اس کی طبعی اہمیت کیا ہے؟ -6

Ans: ΔH is the enthalpy change and q_p is amount of heat supplied at constant pressure. This equation shows that the expansion (پھیلاؤ) of the gas takes place at constant pressure and work is done by the system.

Q.7 What is the comparison of ΔH and ΔE . or State why $\Delta H \approx \Delta E$ in a case of liquids and solids.

(Azad Jammu & Kashmir 2005, Lahore-2006, Rawalpindi 2007, Rwp. 2008, Faisalabad 2010, Faisalabad 2011, Lahore 2012, B. Pure 2013, D.G. Khan 2013, Federal 2013)

ΔH اور ΔE میں کیا فرق ہے؟ بیان کریں کہ مائع اور ٹھوس اشیاء کے لیے ΔH تقریباً ΔE کے برابر کیوں ہوتا ہے؟ -7

Ans: ΔH is the energy change when the pressure is constant (حساب پر پشر مستقل ہو) and ΔE is the energy change when volume is constant. So ΔE can be measured for gases, liquids and solids by keeping volume constant in gases. The volumes of liquids and solids are already constant (پہلے ہی مستقل ہیں). Pressure has no effect on the liquids and solids, so the value of ΔH and ΔE is same for liquids and solids.

Q.8 The total energy of a system is the sum of translational, rotational and vibrational motions. Justify it. (Model Paper-2006-07, B. Pure 2012)

اس کو صحیح ثابت کریں کہ کسی سسٹم کی کل انرجی اس کی جگہ بدلنے، گھومنے اور ارتعاشی حرکت والی انرجی کے مجموعے کے برابر ہوتی ہے؟ -8

Ans: The substances are consisted of atoms, ions and molecules. If a system is in liquid or gaseous state, then its constituent particles (جزوی ذرات) have translational motions (جگہ بدلانے والی حرکت) along three axis x, y and z in space. They need energy for this.

For rotational motions (گھومنے کی حرکت) along three axis they also need energy. Various types of vibrational motions (ارتعاشی حرکت) of the bonds make the bonds to compress (دبا جانا) and stretch (کھلنا). They also demand (ضرورت رکھتے ہیں) energy. So the total energy of a system is a sum of all these three types of energies.

First law of thermodynamics

Q.9 State first law of thermodynamics and give its mathematical form.

(Rawalpindi 2005, Lahore 2007, Rwp. 2009, Fd. 2009, Rwp 2011)

حرکیات کا پہلا قانون بیان کریں اور اس کی مساوات بھی لکھیں۔ -9

Ans: According to the first law of thermodynamics (حرکیات کا پہلا قانون), energy can neither be created nor destroyed. If a gas is enclosed (بند ہے) in a piston cylinder arrangement and it is heated by giving some calories of energy, then the piston

can be pushed (دھکیلتا) to the backward direction. So some of the heat is converted (تبدیل ہوتی ہے) into internal energy and other is used up to do the work. So

$$dq = dE + dW$$

Since $dw = -ve$

$$so \quad dq = dE - dw$$

This equation gives us quantitative relationship (مقداری تعلق) of heat and work.

Q.10 How do we determine the ΔH in the laboratory for food, fuel etc.?

(Model Paper, Lahore 2012)

-10 خوراک یا کسی ایندھن وغیرہ کے لیے ΔH کو لیبارٹری میں کیسے نکالتے ہیں؟

Ans: For this purpose, bomb calorimeter is used. The substance under test is ignited electrically (بھکی سے جلاتا) in the atmosphere of oxygen (O_2 کی فضا میں). The amount of heat produced is calculated from the mass of the substance (چیز کی کیت سے), specific heat (درجہ حرارت کی تبدیلی سے) of the calorimeter and change of temperature (حرارت مخصوص).

Q.11 How will you differentiate between ΔE and ΔH ? Is it true that ΔH and ΔE have the same values for the reactions taking place in the solution state.

-11 آپ ΔH اور ΔE میں کیسے فرق بیان کریں گے؟ کیا درست ہے کہ وہ تعاملات جو سولیوشنز میں ہوتے ہیں ان کی ΔE اور ΔH کی قیمتیں برابر ہوتی ہیں؟

Ans: ΔH is the heat change at constant pressure, while ΔE is the heat change at constant volume. In the solution state the pressure is constant (سولیوشنز میں تعاملات کے) (دوران پریشر مستقل رہتا ہے). So, there is no difference in ΔE and ΔH in such situation (ان حالات میں). There is no change in volume when the reaction happens in liquid or solid state.

Hence,

$$P\Delta V = 0$$

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P \times 0$$

$$\Delta H = \Delta E$$

Q.12 Specific heat of a substance depends upon the nature of substance. Comment.

-12 کسی چیز کی حرارت کو جذب کرنے کی صلاحیت اس چیز کی فطرت پر انحصار ہوتی ہے۔ اس پر بحث کریں۔

Ans: Specific heat (خاص قسم کی حرارت) is the amount of heat required to raise the temperature of 1 g of substance by 1 kelvin. The specific heat of H_2O is $4.2 \text{ J g}^{-1} \text{ K}^{-1}$, while for ethanol it is $2.4 \text{ J g}^{-1} \text{ K}^{-1}$. Actually, it is the capability (صلاحیت) of the substance to possess certain amount of energy. This capability depends upon the structure (ساخت), bond angles and vibrational frequencies (ارتعاشی تعدد) of the bonds etc.

Lattice energy

Q.13 How the lattice energy of the ionic compound can be measured by Born-Haber cycle? (Bahawalpur Board 2005)

-13 یورن۔ ہائر سائیکل کس طریقے سے کسی آئٹک مرکب کی لیٹس انرجی نکالنے میں مدد دیتا ہے؟

Ans: We first of all determine heat of formation of compound in laboratory. The heat of sublimation (عمل تسعید کے لئے حرارت), heat of ionization, amount of electron affinity, bond dissociation energy (بانڈز توڑنے کی انرجی), are consulted from the book. The sum of all these energies and lattice energy of the substance are equalized (برابر کرنا) with heat of formation

$$\Delta H^{\circ}_f = \Delta H^{\circ}_s + \Delta H^{\circ}_i + \Delta H^{\circ}_{D/2} + \Delta H^{\circ}_E + \Delta H_l$$

Q.14 How the amount of lattice energy of an ionic compound depends upon the charge densities of the ions?

(Model Paper-2006-07, Rawalpindi 2007, Lahore 2007)

-14 کسی آئٹک مرکب میں کس طرح سے لیٹس انرجی اس کے آئٹز کے چارج کی کثافت پر منحصر ہے؟

Ans: Lattice energy (ڈھانچہ کو جوڑنے والی انرجی) is the quantitative measurement of forces of attraction among the ions. Greater the amount of charge on positively charged ion, greater the forces of attractions and greater is the lattice energy. Greater the size of negative ion, smaller the charge density and smaller the lattice energy with a definite positive ion.

Q.15 Define lattice energy and give examples.

(Multan 2008, Rwp. 2010, F. Abad 2012, Lahore 2014)

-15 لیٹس انرجی کی تعریف کریں اور دو مثالیں دیں۔

Ans: The energy required to completely separate (مکمل طور پر الگ کرنا) a mole of a solid ionic compound into its gaseous ions is called lattice energy. The lattice energy of NaCl is -787 kJ mol^{-1} .

Q.16 What is heat of atomization? (Rwp. 2010, Guj. 2013)

-16 کسی مرکب کے ایٹمز کو الگ الگ کر دینے کی حرارت کیا ہوتی ہے؟

Ans: It is the amount of heat required to break all the bonds in one mole of a compound to get the atoms.

Q.17 Burning of a candle is a spontaneous process. Justify.

(Guj. 2010, R. Pindi 2012, M. Pure 2012)

-17 موم بتی کا جلنا ایک خود بخود ہونے والا عمل ہے۔ درست ثابت کریں۔

Ans: Candle needs the required temperature from outside. Then the heat evolved due to burning makes the reaction spontaneous.

Q.18 It is true that a non-spontaneous process never happens in the universe

(Rwp. 2010, Guj. 2012, B. Pure 2013)

-18 کیا یہ صحیح ہے کہ خود بخود نہ ہونے والے عملیات کائنات میں کبھی نہیں ہوتے؟

Ans: ΔG is the free energy change (فری انرجی میں تبدیلی) of a reaction and $\Delta G = \Delta H - T\Delta S$. In a spontaneous process, ΔG is negative. To make it negative, the values and signs of ΔH and ΔS decide.

A non-spontaneous process (اپنے آپ نہ ہونے والا عمل) cannot happen in the universe if ΔG is positive for it. Sometimes, we have to supply energy from outside to make them happen (ان کو کرنے کے لئے باہر سے انرجی دینی پڑتی ہے).

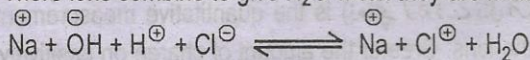
Q.19 Describe Hess's Law of constant heat summation.

(Lahore 2013, Guj. 2013, Faisalabad 2013)

Ans: The energy change in a cyclic process is zero. The heat change of a reaction does not depend upon the path taken. The conversion of carbon and oxygen into CO_2 completes through a single step or two steps. The value of ΔH i.e., $-393.7 \text{ kJ mol}^{-1}$ remains the same.

Q.20 Enthalpy of neutralization of a strong acid and a base is $-57.5 \text{ kcal mol}^{-1}$. Why? (D.G. Khan 2014, Guj. 2014)

Ans: A strong acid and a strong base are completely dissociated in water to give H^+ and OH^- . These ions combine to give H_2O when they are mixed.



$$\Delta H = -57.5 \text{ kcal mol}^{-1}$$

Q.21 Prove that $q_p = \Delta H$.

(Guj. 2014)

Ans: Since $q = \Delta E + W$

$$W = P\Delta V$$

$$q_p = \Delta E + P\Delta V$$

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$q_p = (E_2 + PV_2) - (E_1 + PV_1)$$

$$q_p = H_2 - H_1$$

$$q_p = \Delta H$$