

## Calculation Of Heat Content And Entropy Of Polyethylene

Thamir Salman Bachari

Polymer Research Centre, Material science Department, University  
of Basrah

### Abstract:-

Calculation of heat content and entropy have been done for polyethylene for different chain length, are reviewed with support of data obtained from the thermo-chemical and thermodynamic for monomer unit and polyethylene, by using equations expressing these proportions at 25°C as a function of n, which is the number of ethylene units per polymer molecule, for gaseous state of monomer unit of ethylene to a narrow chain of polyethylene. We have reviewed for n the number monomer units per polymer molecule for  $n \geq 2$ ,  $n \geq 4$  and for (mono-olefin)  $n \geq 3$ , and at large numbers of n.

### Introduction:

The value of heat content  $\Delta H_x^\circ$  and entropy  $\Delta S_x^\circ$  are for 25°C when monomer is only partially polymerized, depend on the contribution concentration of polymer is also be stipulated since there will be small contribution which may vary with dilution  $\Delta H^\circ$  and  $\Delta S^\circ$ <sup>[1]</sup>. From the heat and entropy per mole of monomer polymerized under various conditions is specified. Experimental methods for determining heats of polymerization are reviewed and the magnitude of various phase change corrections discussed in relation to existing data on mono-olefin<sup>[2]</sup>. Various empirical method of evaluating  $n\Delta H_{\text{EE}}^\circ$ , which is a hypothetical quantity from gaseous to gaseous state of polyethylene are out lined and use made of Anderson, Beyer and Watson's group method to calculate values of its quantity over range of temperature for ethylene<sup>[3]</sup>, un-conjugated vinylidene compounds and styrene. The method for measuring entropies of polymerization are described namely from equilibrium or "ceiling temperatures" and from standard entropies of polymer and monomer<sup>[4]</sup>. Empirical and statistical methods are outlined and phase change corrections and probable effects of monomer and polymer are described. Finally, the magnitude of the ratio  $\frac{\Delta H^\circ}{\Delta S^\circ}$  of high polymerization and its temperature variation, are outlined<sup>[5]</sup>. These equations will usually increase with chain length, n, to limiting values when, n, is small. When n is large be used on prefix, e.g. n is large  $\Delta H_{\text{EE}}^\circ$  and  $\Delta S_{\text{EE}}^\circ$  are hypothetical quantities,  $\Delta H^\circ$  and  $\Delta S^\circ$  will also vary with temperature, but this effect is found to be slight and in the same sense for both quantities and there for found to be slight and the ratio  $\frac{\Delta H^\circ}{\Delta S^\circ}$  to be slightly

depend on temperature and hence the ceiling temperature may be put approximately equal to this ratio at 25°C, the ceiling temperature obtained by  $\frac{\Delta H_x}{\Delta S_x} = T_x$  [6],  $\Delta H_x$ ,  $\Delta S_x$  are increment of  $T_x$  of the heat content and entropy per mole of monomer polymerized [7]. Polymerization is ordinarily considered to be combination of monomer molecules to form larger molecules, each of which contains an integral number of monomer units. It is doubtful, however, that the actual reactions by which polymers are formed are simple as this. At high temperatures, at least, the reaction of polymerization, as defined above, would be expected to be accompanied by degradation reactions going at the same time. Such degradation would be expected to involve, among other things, the breaking of polymer chains at a points far removed from the ends, where there is no distinction between the carbon-carbon bonds of the chain which were originally carbon-carbon bonds in monomer molecules and those which are bonds between adjacent monomer units. Some of the resulting polymer molecules would then contain fragments of the original monomer molecules as well as entire monomer units. In particular, it is to be expected that some polyethylene molecules would contain odd numbers of carbon atoms, that is, half-odd integral numbers of ethylene units. In accordance with these considerations, the term "polymerization" is here used to mean the process by which ethylene molecules react to form larger normal mono-olefin molecules, which may contain either even or odd numbers of carbon atoms [8].

### **Method:**

The method by which heats of polymerization can be determined can be found by the methods: The main method is based on the relation:

$$\Delta S_x^\circ = \frac{\Delta H_x^\circ}{T_x}$$

is only limited by the accuracy of calculation of heats of polymerization, the ceiling temperature is determined by heat change and one equilibrium temperature, since  $\Delta H$  is well found below ceiling temperature. An actual temperature-heat content and reciprocal temperature –entropy graphs are plotted. And the method in which  $M_1$  are calculated on range of temperatures applying equation [4] in the theory. and  $K$  can be calculated applying equation of the form:

$$K = \frac{(M_n)^{\frac{1}{n}}}{(M_1)}$$

since  $M_n$  is constant[op.cit[4]], The method based on the determination of sublimation pressures from the graph of  $\Delta H$  of gaseous polyethylene with temperatures in the range (200-300)°C,  $\Delta H$  can

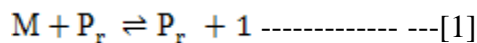
be calculated using equation of the form:

$$\Delta H = \Delta C_p \int_{T_1}^{T_2} dT$$

$\Delta C_p$  can be calculated applying equation [5] as will be applied for the above range of temperatures.

THEORY:

The kinetic analysis of the region of ceiling temperature for a polymerization reaction in which the property ion-step:



M : denotes monomers,  $P_r$  growing polymer of length r, the rate appreciable reversal of the reaction is occurring will be given by the rate of reaction where appreciate.

By application of the isochors to the over- all equilibrium is evident that:

$$\frac{d \ln(M)}{dT} = - \frac{\Delta H_x^\circ}{RT^2} \text{ ----- [2]}$$

Entropy is constant of the system. This later condition is satisfied when the polymer exists or pre condensed. In order to obtain the value of S over range of temperature[op.cit [7]]:

$$T_x = \frac{\Delta H_x^\circ}{(\Delta S_x^\circ + R \ln(M_1))} \text{ ----- [3]}$$

$\Delta S$  here refer to 1 mole. Liter<sup>-1</sup>.

$$\ln(M_1) = - \frac{\Delta H_x^\circ}{RT^2} \text{ ----- [4]}$$

$\Delta H_x^\circ$  and  $\Delta S_x^\circ$  are substatically invariant and T is the ceiling temperature for the monomer concentration  $[M_1]$ . In the special case when the polarize polymerizability, depolymerized to equilibrium may be approved from the polymer side<sup>[A]</sup>.

Return to the hypothetical quantities, we have use equation of the form;

$$\Delta H = \Delta H_{298} - \int_{298}^T C_p(R) dT + \int_{298}^T C_p(P) dT + \Delta H_{V_{\alpha\beta}} + \int_{T_2}^{T_1} C_p(P) dT \cdot$$

In which R, P refers to reactants and products and p pressure [op.cit[3]]. And  $\Delta$  is the electronegativity difference[op.cit(5)].

The heat capacity of gases of temperature such as<sup>[B][C]</sup>;

$$C_p = a + b \cdot T + c \cdot T^2.$$

a, b and c are constant for particular material.

$$\Delta C_p = \Delta a + (\Delta \frac{b}{2}) \cdot T^2 + (\Delta \frac{c}{3}) \cdot T^3 \cdot \text{ ----- [5], Then we have use the empirical equation;}$$

$$\int_{298}^T d(\Delta H) = \int_{298}^T \Delta C_p dT = \int_{298}^T (\Delta a + \Delta b^*T + \Delta C^*T^2) dT \quad \text{-----}[5^*]$$

$$\Delta H = \Delta H^\circ + \Delta a^*(T - 298) + \Delta \frac{C^*}{2} (T^2 - 298^2) + \Delta \frac{C^*}{3} (T^3 - 298^3) \quad \text{-----}[6]$$

For large values of n, we have the empirical equation:

$$n\Delta H_{\text{EE}}^\circ(T) = n\Delta H_{\text{EE}}^\circ(25^\circ\text{C}) + \Delta a^* (T - 298) + \Delta \frac{C^*}{2} (T^2 - 298^2) + \Delta \frac{C^*}{3} (T^3 - 298^3) \quad \text{---}$$

[7]

The methods for evaluating  $n\Delta S_{\text{EE}}^\circ$  empirically are in principles the same as those for the estimation of  $n\Delta H_{\text{EE}}^\circ$ . The values of  $n\Delta S_{\text{EE}}^\circ$  may then be obtained in the usual way, appropriate to  $n \rightarrow \infty$ .

$$\int_{298}^T d(\Delta S) = \int_{298}^T \frac{C_p}{T} dT = \int_{298}^T \frac{(\Delta a + \Delta b^*T + \Delta C^*T^2)}{T} dT, \text{ we can obtain}$$

$$\Delta S_x = \Delta S^\circ + \Delta a^* \ln \frac{T}{298} + \Delta b^*(T - 298) + \Delta \frac{C^*}{2} (T \wedge 2 - 298 \wedge 2) \quad \text{-----}[8]$$

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## RESULTS AND DISCUSSION:

Starting from the equation of heat capacity, the molar heat capacity of selection gases according to the equation[op.cit[B]]:

$$C_p = a + b^*T + C^*T \wedge 2 + d^*T \wedge 3 \quad \text{-----}[10]$$

$C_p$  varies in nonlinear fashion with temperature. The number of terms commonly used to describe varies from two to four. High temperature reactions are becoming increasingly important, and as a result wider variations in  $C_p$  are encounter, so we shall use equation [10] for the calculation of  $C_p$  of ethylene in which  $a, b, C$  and  $d$  are constants.

**Table-1-Molar heat capacity of monomer ethylene according to equation [10]**

compound	a	$10^2 b$	$10^5 C$	$10^9 d$
$C_2H_4$	0.9449	3.7392	-1.9949	4.2248

Units in  $\text{cal.mol}^{-1}.\text{K}^{-1}$ .

$$C_p = 10.42766 \text{ cal.mol}^{-1}.\text{K}^{-1}$$

By applying the equation:

$$\int_{298}^T \frac{d(\Delta H)}{dT} = \Delta C_p .$$

We have the values obtained as in table-2- from equation [5], [7] and [9]. Since we have,

$$\Delta H_{x2} = \Delta H_{x1} + \Delta C_p * \Delta T^*,$$

therefore,  $\Delta S_{x2} = \Delta S_{x1} + \text{constant}^*$ ,

values indicated in table-2-. And the fact that,

$T_x = \frac{\Delta H_x}{\Delta S_x}$  when  $\ln[M] = 0$ , so that  $[M] = 1 \text{ mol.l}^{-1}$ . And applying the equation,

$$K = \frac{(M_n)^{\frac{1}{n}}}{(M_1)},$$

From which the calculated values of **K** as indicated in table-2-, in which n has all values within a very wide range. The unit of  $[M_1]$  was taken 1 mole.l<sup>-1</sup>. From the calculated values in table-2-, the plotted graph between the temperature- heat content as in fig.(1), which is a straight line, and shows that the heat content  $\Delta H_{x2}^\circ$  increase as temperature increase, in agreement with the ceiling temperature equation above. And the reciprocal temperature- entropy graph is plotted fig.(2) which is exothermic curve from which heat is librated and may involve homogeneous initiation (radical or cationic)<sup>[D]</sup>. The temperature-  $[M_1]$  graph fig.(3) is approximately a straight line, Which cut the temperature axis at point, which is equal to 302°C close to the range 200- 300 °C for systems in which the entropy of the polymer is constant<sup>[E]</sup>. From table-3-, the graph as in fig.(4), between temperature and heat content at sublimation, the slop is equal to 0 .003 Kcal.mol<sup>-1</sup>.K<sup>-1</sup>, and by using Clausius-Claperon equation:

$$d \ln \frac{P_2}{P_1} = \frac{\Delta H}{RT^2} \text{ ----- [11]}$$

Whereupon the variables can readily be separated and the equation integrated as follows:

$$\ln \frac{P_2}{P_1} = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2}$$

Finally, if we assume that  $\Delta H$  is constant, we can perform the integration and get

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R(T_1 - T_2)} \text{ ----- [12]}$$

Which is a statement relating to sublimation pressures to the corresponding temperatures. If the integration carried out indefinitely, and the equation can be written in the following form:

$$\ln P = -\frac{\Delta H}{RT} + \text{constant} \quad [13]$$

In which can introduce further refinement naturally, by taking into account the dependence of  $\Delta H$  on temperature by eliminating through various devices some of the other approximation that were made in the derivation<sup>[F]</sup>.

The calculation of sublimation pressure (p) is equal to 0.324 atm., which is 32859.171 N/m<sup>2</sup><sup>[G]</sup>. This is to hypothetical gaseous polymer ( $T_{EE}^{\circ}$ ) should lie in the range 200 – 300° C. Equation [13] in agreement with vapor pressure of most substances. And is approximately valid for evaporation and sublimation<sup>[H]</sup>.

As a rotation about an atoms axis's (again whether the atoms is bound or free) its energy of rotation is proportional to the moment of inertia for the atom, which is extremely small compared to the moment of inertia of collection atoms. This is because almost all of the mass of single atom is concentrated in its nucleus which has radius too small to give significant moment of inertia. In contrast, the spacing of quantum energy levels for rotating objects is inversely proportional to its moment of inertia, so this spacing becomes very large for objects with a very small moment of inertia. For these reasons, the contribution rotation atom on their axis's is essentially zero in monatomic gases, because the energy spacing of the associated quantum level is too large for significant thermal energy to be stored in rotation of a systems such as small moment of inertia in polyatomic molecules, other rotational modes may becomes active, due to the much higher moment of inertia about a certain axis which do not coincide with linear axis of a linear molecule. These modes take the place of some translational degree of freedom atoms, since the atom are moving in 3-D space, as the molecules rotate. Furthermore internal vibration degrees of freedom also may become active (these are also type of translation, as seen from the view of each atom). Molecules are complex object with population of atoms that may move about within the molecule in a number of different ways and each of these ways of moving is capable of storing energy if the temperature is sufficient<sup>[I]</sup>.

## **Conclusions:**

Chain- growth polymerization which initiated by reactive species, can be divided into free-radical anionic and cationic polymerization. The reactive species adds to monomer to form a new active center successively. This process is called propagation reaction. In general the propagation reaction is represented by equation[1]. In chain- growth polymerization, only molecules with active centers can propagate; so that polymer molecules once formed may be considered dead polymer for linear chain-growth polymerization. Dead polymer molecules do not take part as reactants thereafter. The active center is always on the chain and when linear chains are being produced exclusively<sup>[J]</sup>. The heats and entropies of formation of gaseous organic compounds in the standard state and coefficients in the specific heat-temperature equation have been resolved into contributions attributable to atomic group.  $\Delta C_p$  is necessary in order to obtain the values of  $\Delta S$  over a range of temperatures. Since both  $\Delta H_x^{\circ}$ ,  $\Delta S_x^{\circ}$  are a functions of temperature as in eqn. [7] and [9] an increase of  $\Delta H_x^{\circ}$  with temperature is always

associated with an increase of  $\Delta S_x^\circ$ ; these two effects are of such a magnitude that the ratio of  $\Delta H_x^\circ/\Delta S_x^\circ$  at 25°C is very slightly different [ table -2-], columns [2] and [6], columns [5] and [9] are an evidence which is equal to this ratio at 25°C. Polyethylene can serve as standard material for the thermodynamic functions of a simple linear macromolecule<sup>[K]</sup>. The empirical method for computing  $\Delta H_{EE}^\circ$  and  $\Delta S_{EE}^\circ$  at temperature  $[T_{EE}^\circ]$  in the range 200-300°C, calculated sublimation pressure [p] is 0.324 atm. Entropy comes from the second law of thermodynamics, which states that all systems tend to reach a state of equilibrium. The significance of entropy is that when a spontaneous change occurs in a system, it will be found that if the total entropy for everything involved is calculated, a positive value will be obtained. Simply, all spontaneous changes in an isolated chemical system occur with an increase in entropy. Entropy like heat content is also a state property and is represented by the symbol "S" and can be used to calculate the change in entropy ( $\Delta S$ )<sup>[L]</sup>.

**Table-2- The calculation of heat content and entropy according to equation 5\*, 7, 9 and eqn. Under\***

$(\Delta T_{EE}^\circ)$ K	$\Delta H_{x1}^\circ$ Kcal. mol <sup>-1</sup>	$\Delta H_{x2}^\circ$ Kcal. mol <sup>-1</sup>	$\Delta H_{EE}^\circ$ (T)kcal. mol <sup>-1</sup>	$\Delta H_{EE}^\circ$ (25°C)Kcal l. mol <sup>-1</sup>	$\Delta S_{x1}^\circ$ Kcal .mol <sup>-1</sup> .K <sup>-1</sup>	$\Delta S_{x2}^\circ$ Kcal. mol <sup>-1</sup> .K <sup>-1</sup>	$\Delta S_{EE}^\circ$ (T)Kcal. mol <sup>-1</sup> .K <sup>-1</sup>	$\Delta S_{EE}^\circ$ (25°C)Kcal l.mol <sup>-1</sup> .K <sup>-1</sup>
298	3.1084	-----	-----	3.108	0.0104	-----	-----	0.0104
473	-----	1.824	4.933	3.109	-----	0.0166	0.0298	0.0210
483	-----	1.929	5.037	3.108	-----	0.0169	0.0273	0.0104
493	-----	2.033	5.147	3.114	-----	0.0172	0.0278	0.0108
503	-----	2.137	5.246	3.109	-----	0.0176	0.0280	0.0104
513	-----	2.241	5.350	3.109	-----	0.0179	0.0283	0.010
523	-----	2.346	5.454	3.108	-----	0.0183	0.0287	0.0104
533	-----	2.450	5.558	3.108	-----	0.0186	0.0290	0.0094
543	-----	2.554	5.663	3.109	-----	0.0196	0.0294	0.0098
553	-----	2.659	5.767	3.108	-----	0.0193	0.0297	0.0104
563	-----	2.763	5.871	3.108	-----	0.0197	0.0301	0.0104
573	-----	2.867	5.976	3.109	-----	0.0200	0.0304	0.0104

**Continue table-2-**

M1 mol.l <sup>-1</sup>	Mn mol.l <sup>-1</sup>	K(n≥2)	K(n≥3)	K(n≥4)	K(n≥11)	K(Large) n≥40)
0.1434	0.0057	0.5287	1.2456	1.9202	4.3595	6.1284
0.1339	0.0057	0.566	1.3340	2.0557	4.6688	6.5632
0.1254	0.0057	0.6046	1.4244	2.1959	4.9852	7.0064
0.1176	0.0057	0.6448	1.5193	2.3415	5.3159	7.4684
0.1108	0.0057	0.6843	1.6121	2.4846	5.6422	7.9293
0.1045	0.0057	0.7256	1.7093	2.6351	5.9823	8.4097
0.0988	0.0057	0.7671	1.8070	2.7857	6.3274	8.8903
0.0936	0.0057	0.8096	1.9074	2.9402	6.6790	9.3840
0.0888	0.0057	0.8530	2.0095	3.101	7.0400	9.8865
0.0845	0.0057	0.8969	2.1129	3.2588	7.3982	10.3952
0.0805	0.0057	0.9415	2.2179	3.419	7.7659	10.9115

**Table-3- heat content at sublimation at temperatures indicated.**

TK	$\Delta H$ Kcal.mol <sup>-1</sup>
473	4.020
483	4.153
493	4.486
503	4.828
513	5.196
523	5.543
533	5.863
543	6.353
553	6.746
563	7.150
573	7.449



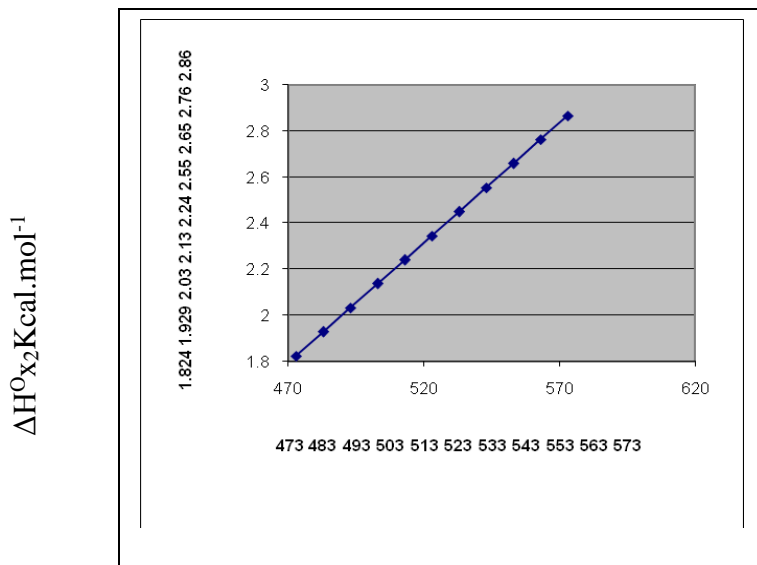


Fig.1. The temperature-heat conte

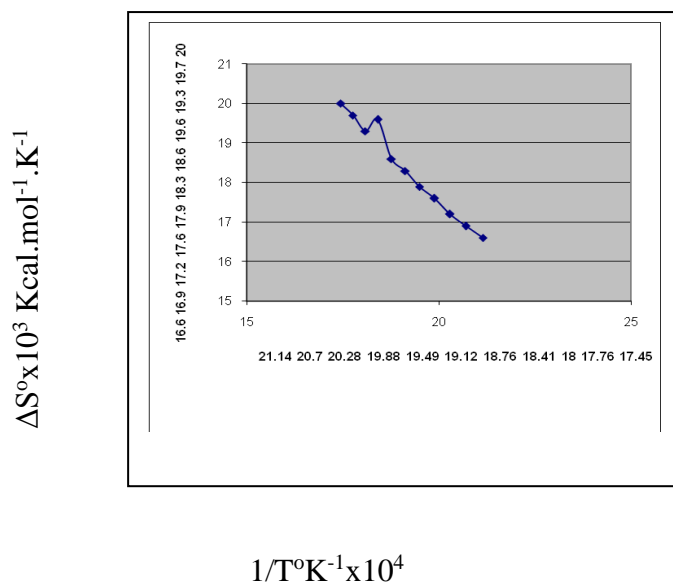


Fig-2- Exothermic plot of temp.-

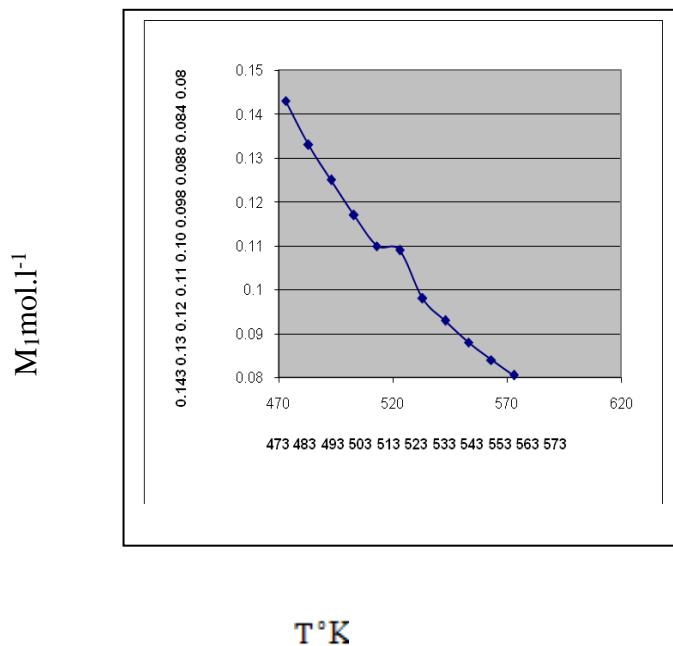


Fig.3. The temperature-rate  $M_1$

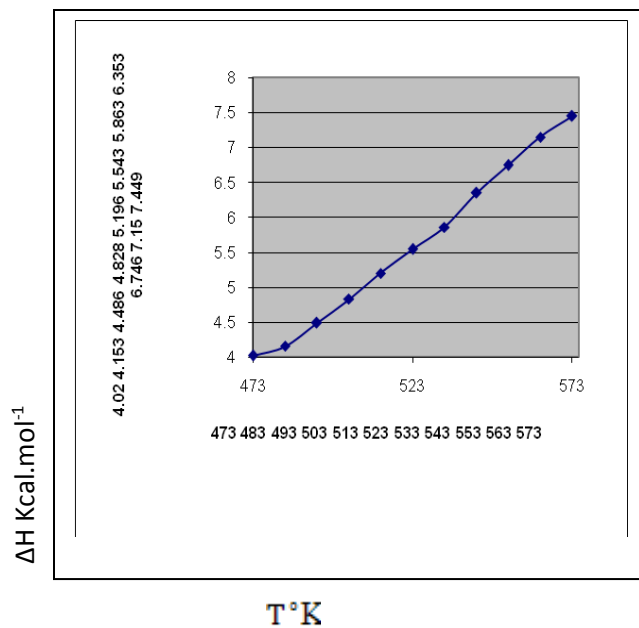


Fig-4- Temperature-  $\Delta H$

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## حساب المحتوى الحراري والانتروبي لمتعدد الأتلين

ثامر سلمان البجاري

مركز أبحاث البوليمر- قسم علوم المواد- جامعة البصرة

### الخلاصة :-

تم حساب المحتوى الحراري لمتعدد الأتلين ذات حزم مختلفة الطول. ودراسة النتائج التي يعززها حقائق مصادر الكيمياء الحرارية والديناميكية الحرارية بالنسبة الى أحادي الوحدة ومتعدد الأتلين، باستخدام معادلات تبين هذه النسب في درجة حرارة 25 م كدالة الى عدد وحدات الأتلين لكل جزيئة بوليمرية (n)، للحالة الغازية لأحادي الوحدة الى حزمة محدودة لمتعدد الأتلين، عندما  $n \geq 2$ ,  $n \geq 4$ , والى أحادي الأوليفين عندما  $n \geq 3$ . وكذلك الدراسة لقيم كبيرة لـ n .