

Combining (V) and (VI), the following equation is obtained:

$$\Delta F = \Delta H_0 - \Delta \Gamma_0 T \ln T - \frac{1}{2} \Delta \Gamma_1 T^2 - \frac{1}{6} \Delta \Gamma_2 T^3 + \dots IT \quad \dots \quad \dots \quad \text{(VII)}$$

where I is the integration constant.

For the derivation of free energy equation, it will be observed that the knowledge of ΔH_0 , I and the heat capacity equation (IV) are essential.

For the evaluation of the values ΔH_0 and I the following methods have been used:—

(1) When the equilibrium data were available, the value of ΔH_0 was directly calculated by employing the equation:

$$\frac{\partial \ln k}{\partial T} = \frac{\Delta H_0 + \Delta \Gamma_0 T + \frac{1}{2} \Delta \Gamma_1 T^2 + \frac{1}{3} \Delta \Gamma_2 T^3}{RT^2} \quad \dots \quad \dots \quad \dots \quad \text{(VIII)}$$

(2) When the data for the heat of combustion for the products and reactants at standard state were available, ΔH_0 was calculated from equation (V). In the case of the isomers like butene-1 and butene-2 (cis and trans) the difference in the heats of formation was evaluated from the hydrogenation data since the difference in the heats of hydrogenation, when the reaction is clear cut and the hydrogenated product is the same for two or more unsaturated hydrocarbons, gives the difference in the heats of formation for all these hydrocarbons.

(3) For the evaluation of I , when ΔH_0 was known, the value for ΔF_T at one definite temperature was required. This has been calculated by the following two methods:—

(i) From the knowledge of the equilibrium constant for the reaction, ΔF_T has been calculated from the well-known equation:

$$\Delta F_T = -RT \ln K_p \quad \dots \quad \dots \quad \dots \quad \text{(IX)}$$

(ii) When the entropy change, ΔS_T and the heat of reaction, ΔH_T could be obtained from the calorimetric and spectroscopic data, the value of ΔF_T was calculated from the equation:

$$\Delta F_T = \Delta H_T - T \Delta S_T \quad \dots \quad \dots \quad \dots \quad \text{(X)}$$

The Specific Heat Equation: To derive a satisfactory equation expressing the free energy of reaction as a function of temperature, it is essential to know equations accurately representing the specific heat of the reactants and the products over the temperature range considered. Direct heat capacity measurements for these hydrocarbons are almost completely lacking. The only data available for the derivation of the specific heat equation for some of the hydrocarbons is the spectroscopic work of Beeck (1). Employing Beeck's data, Thomas, Egloff and Morrell (2) have calculated the specific equations for some of the lower paraffins and olefins.

Specific heat equation for the Dehydrogenation of paraffins to olefins:

Using the following heat capacity equations of hydrogen, carbon, *n*-butane and butene-1,

$$\text{Hydrogen: } C_p = 6.890 - 0.000,114T + 0.000,000,444T^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(1) [3]}$$

$$\text{Carbon (graphite): } C_p = 1.1 + 0.0048T - 0.000,001,2T^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(2) [4]}$$

$$\textit{n-Butane: $C_p = 4.64 + 0.0558T \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(3) [2]}$$$

$$\text{Butene-1: } C_p = 4.61 + 0.0513T \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(4) [2]}$$

we obtain the following ΔC_p equation for the formation of *n*-butane and butene-1, from the elements:

$$\textit{n-Butane: $\Delta C_p = -34.21 + 0.0372T + 0.000,0024T^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(5)}$$$

$$\text{Butene-1: } \Delta C_p = -27.35 + 0.0326T + 0.000,003T^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(6)}$$

By subtracting equation (5) from (6), we obtain the following specific heat equation for the dehydrogenation of *n*-butane to butene-1.

$$\Delta C_p = 6.86 - 0.0046T + 0.000,000,6T^2 \quad \dots \quad \dots \quad \text{(XI)}$$

Specific Heat Equation for the Dehydrogenation of Mono-olefins to Diolefins: Thomas, Egloff and Morrell (2) have computed the specific heat equation for butadiene-1,3 by the following scheme:—

$C_p = \frac{5}{2}R$ (translation) + $\frac{3}{2}R$ (external rotation) + $\frac{1}{2}R$ (internal rotation) + vibration and have arrived at the equation:

$$\text{Butadiene-1,3: } C_p = 11.6 + 0.0448T.$$

The above equation as will be seen, represents unusually high value for C_p and it is improbable that a molecule of butadiene-1,3 which is formed through the dissociation of a molecule of hydrogen from butene, should have such high heat capacity. If we however assume the above C_p equation for butadiene-1,3, the following ΔC_p equation for the dehydrogenation of butene-1 to butadiene is obtained:

$$\Delta C_p = 13.88 - 0.0036T + 0.000,0005T^2 \quad \dots \quad \text{(XII)}$$

On comparing the equation (XII) with the corresponding equation (XI) for the dehydrogenation of *n*-butane to butene-1, a large difference will be observed, which is unlikely because both the equations are for the dehydrogenation process involving dissociation of a molecule of hydrogen in each of the two successive reaction steps. In the absence of any other data the equation (XI) based upon comparatively reliable spectroscopic data, has been assumed as a general specific heat equation for the dehydrogenation processes involved in the formation of olefins from paraffins and diolefins from olefins of the *n*-butane and isopentane series.

Heat of formation from Calorimetric Data: The values for the heats of formation from solid carbon (graphite) and gaseous hydrogen of the following paraffins, olefins and the diolefin butadiene-1,3 (Table I), calculated by Rossini (5), have been employed in the present calculations.

TABLE I.

Heats of formation of gaseous hydrocarbons from solid carbon (graphite) and gaseous hydrogen at 25°C.

Hydrocarbons.	Formula and state.	$\Delta H^\circ_{298.1}$ cal. per mole.
<i>Paraffins :</i>		
<i>n</i> -Butane	C_4H_{10} (g)	$-29,715 \pm 153$
Iso-pentane	C_5H_{12} (g)	$-36,671 \pm 153$
<i>Olefins :</i>		
Butene-1	C_4H_8 (g)	383 ± 180
Cis-butene-2	C_4H_8 (g)	$-1,388 \pm 180$
Trans-butene-2	C_4H_8 (g)	$-2,338 \pm 180$
2-Methyl-butene-1	C_5H_{10} (g)	$-8,424 \pm 200$
3-Methyl-butene-1	C_5H_{10} (g)	$-6,578 \pm 180$
2-Methyl-butene-2	C_5H_{10} (g)	$-9,995 \pm 180$
<i>Diolefins :</i>		
1,3-Butadiene	C_4H_6 (g)	$26,865 \pm 240$
1,3-Methyl-butadiene or Isoprene	C_5H_8 (g)	No data available.

Entropy from Calorimetric and Spectroscopic data: Entropy of only a small number of hydrocarbons have been so far determined by direct heat capacity measurements. The entropy of *n*-butane, in liquid state at 25°C. was determined by Parks and co-workers (7) by the third law but their heat capacity measurements are limited only to liquid air temperatures. Ewell (8) has converted liquid entropy of *n*-butane to standard state vapour entropy

$$n\text{-butane: } S^\circ_{298.1} = 74.5.$$

Among the olefins, the entropies of cis-butene-2 and trans-butene-2 have been measured by Todd and Parks (9). For butene-1, their measurements were unsuccessful since butene-1 did not get crystallised even at the liquid air temperature. The experimental values are:

$$\text{Cis-butene-2: } S_{298.1} = 74.2$$

$$\text{Trans-butene-2: } S_{298.1} = 72.2.$$

Recently Pitzer (10) has evaluated entropies of *n*-butane, iso-pentane and butenes by employing the statistical method of calculation. These values are given in Table II.

TABLE II.
Molal Entropy and Entropy of Formation from elements at 25°C.

Substances.	S° ₂₉₈₋₁	ΔS° ₂₉₈₋₁
<i>n</i> -Butane	74.1	-87.5
Iso-pentane	82.0	-112.2
Butene-1	75.3	-55.1
Cis-butene-2	73.5	-56.9
Trans-butene-2	72.9	-57.5

In the absence of any other data, the work of Ewell (8) has been found very useful for the present calculations. From a critical review of the available data on entropies of hydrocarbons, he has deduced certain simple rules which permit evaluation of entropies of many straight chain and branched chain paraffins and olefins. Thus from the estimated entropies of methyl-butenes by Ewell, the following values of ΔS_T have been calculated and tabulated in Table III:—

TABLE III.

Substances.	S° ₂₉₈₋₁	ΔS° ₂₉₈₋₁
2-Methyl-butene-1 ..	80.3	-82.7
3-Methyl-butene-1 ..	80.3	-82.7
2-Methyl-butene-2 ..	78.5	-84.5

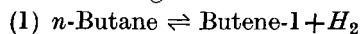
Data from Equilibrium Measurements: In the present calculations the only equilibrium data used, are from the studies on the formation of butadiene-1,3 from butene-1 and isoprene from 3-methyl-butene-1, reported in Parts I and IV. Frey and Huppy (6) have determined the equilibrium constants for the formation of butene-1, cis-butene-2 and trans-butene-2 from *n*-butane. These data have not been used because the free energy equations for these reactions, derived from the recent calorimetric and spectroscopic data have been found to yield much more accurate values than those available from their equilibrium data:

Calculations.

Dehydrogenation Equilibrium in the *n*-butane series.

Paraffin-olefin isomers.

The following derivations are based upon calorimetric and spectroscopic data:—



From Table I, *n*-Butane: $\Delta H_{298} = -29715$ cal.

Butene-1: $\Delta H_{298} = 383$ cal.

Therefore ΔH_{298} for the reaction = 30,098 cal.

Using the specific heat equation (XI) and substituting the value of ΔH_{298} in equation (V), we have $\Delta H_0 = 28,252$ cal.

Hence, $\Delta H_T = 28,252 + 6.86T - 0.0023T^2 + 0.000,000,2T^3$

From Table II, ΔS_{298} for the reaction = 32.4 E.U.

Employing the relation, $\Delta F_T = \Delta H_T - T \Delta S_T$, we have $\Delta F_{298} = 20,442$ cal.

Substituting the values of ΔF_{298} and ΔH_0 in equation (VII) one obtains, $I = 12.21$.

Hence the general equation for standard free energy of the reaction may be expressed as:

$$\Delta F_{298} = 28,252 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 12.21T.$$

The temperature of neutral equilibrium for the reaction is:

$$T_0 = \frac{\Delta H_{298}}{\Delta S_{298}} = 656^\circ\text{C.}$$



From Table I, we derive $\Delta H_{298} = 28,327$ cal. and $\Delta H_0 = 26,481$ cal. Hence the equation for the heat of reaction is:

$$\Delta H_T = 26,481 + 6.86T - 0.0023T^2 + 0.000,000,2T^3$$

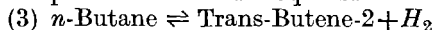
From Table II, we have $\Delta S_{298} = 30.6$ E.U.

Using equation (X), we evaluate $\Delta F_{298} = 19,207$ cal.

This permits derivation of the following free energy equation:—

$$\Delta F_T = 26,481 - 6.86 T \ln T + 0.0023T^2 - 0.000,0001T^3 + 14.01T$$

The temperature of neutral equilibrium = 653°C .



Following the above procedure of calculation, we derive the following thermodynamic functions for this reaction:—

$$\Delta H_{298} = 27,377 \text{ cal.}, \Delta S_{298} = 30.0 \text{ E.U. and } \Delta F_{298} = 18,437 \text{ cal.}$$

These data permit derivation of the equation:

$$\Delta F_T = 25,531 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 14.6T.$$

The temperature of neutral equilibrium = 639.6°C .

Olefin isomers—Diolefins.



Equilibrium data for this reaction is given in Part I. Assuming the specific heat equation (XI), and substituting the following two values of the equilibrium constants,

$Kp = 0.000,82$ at 683°K ; $Kp = 0.004,70$ at 743°K , in the equation (VIII), we evaluate $\Delta H_0 = 25,496$ cal.

After appropriate substitutions in equation (VII), we have

$$\Delta F = 25,496 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 1T$$

In order to evaluate the value of I , we have used $\Delta F_T = 7811$ cal. at 743°K . from the equilibrium data. This gives, $I = 20.03$. Hence, the standard free energy equation for the reaction is given by $\Delta F_T = 25,496 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 20.03T$.

As a check upon the validity of the above free energy equation, the five values of ΔF_T , corresponding to the temperatures at which the equilibrium constants were determined, have been calculated [Part I]. These on comparing with the values of ΔF_T (Table IV), directly calculated from the equilibrium data, show a close agreement.

TABLE IV.

No.	ΔF_T ; cal.	$\Delta F_T = -RT \ln Kp$	Temperature $^\circ\text{C}$.
1	10,620	10,770	643
2	9,642	9,637	683
3	8,748	8,779	713
4	7,911	7,905	743
5	7,294	7,044	773

From the general equations for ΔH_T and ΔF_T , we obtain

$$\Delta H_{298} = 27,342 \text{ cal.}, \Delta F_{298} = 20,015 \text{ cal.}, \text{ and } \Delta S_{298} = 24.6 \text{ E.U.}$$

In order to evaluate the corresponding free energy equations for the dehydrogenation of the two other isomers of butene-1 namely, cis-butene-2 and trans-butene-2 the additional data necessary are: (1) the knowledge of the differences in the heats of formation among the isomers and (2) the free energy of formation of butadiene-1,3.

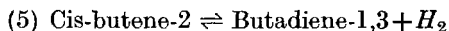
The differences in the heats of formation among the isomers can be readily obtained from the data given in Table I.

For the calculation of ΔF_{298} for butadiene-1,3 the following procedure has been adopted. From equilibrium data, ΔF_{298} for the dehydrogenation of butene-1 to butadiene-1,3 = 20,015 cal.

From calorimetric data,

$$\Delta F_{298} \text{ for the formation of butene-1 from the elements} = 16,810 \text{ cal.}$$

Now, by adding up the above two values, the free energy for the formation of butadiene-1,3 is obtained: $\Delta F_{298} = 36,825$ cal.



The difference in the heats of formation between butene-1 and cis-butene-2 = 1771 cal. at 25°C. (Table I).

From equilibrium data, ΔH_{298} for the dehydrogenation of butene-1 to butadiene = 27,342 cal.

These gives, ΔH_{298} for the reaction = 29,113 cal.

Using, cis-butene-2: $\Delta F_{298} = 15,570$ cal.

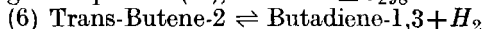
Butadiene-1,3: $\Delta F_{298} = 36,825$ cal.

one obtains, ΔF_{298} for the reaction = 21,255 cal.

Now by the usual method of derivation, we obtain the following free energy equation:

$$\Delta F_T = 27,267 - 6.86T \ln T + 0.0023T^2 - 0.000,000,1T^3 + 18.25T.$$

Using the equation (X), we have $\Delta S_{298} = 26.47$ E.U.



The difference in the heats of formation between butene-1 and trans-butene-2 = 2763 cal.

Therefore, $\Delta H_{298} = 30,105$ cal.

From, Trans-butene-2: $\Delta F = 14,800$ cal.

Butadiene-1,3: $\Delta F = 36,825$ cal.

we have $\Delta F_{298} = 22,025$ cal and $I = 17.5$.

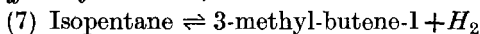
Hence, the free energy equation:

$$\Delta F_T = 28,259 - 6.86T \ln T + 0.0023T^2 + 0.000,0001T^3 + 17.5T.$$

and entropy value for the reaction: $\Delta S_{298} = 27.12$ E.U.

Dehydrogenation Equilibrium in the Isopentane Series.

Paraffin-olefin isomers,



No equilibrium data are available.

Calorimetric data: From Table I, ΔH_{298} for the reaction = 30,093 cal. Employing the specific heat equation (XI), one obtains

$$\Delta H_T = 28,247 + 6.86T - 0.0023T^2 + 0.000,000,2T^3$$

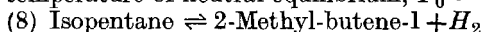
From Tables II and III, ΔS_{298} for the reaction = 29.5 E.U.

And using the equation (X), we have $\Delta F_{298} = 21,303$ cal.

These data permit derivation of the following equation for free energy of the reaction:—

$$\Delta F_T = 28,247 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 15.12T.$$

The temperature of neutral equilibrium, $T_0 = 743^\circ\text{C}$.



From Table I, ΔH_{298} for the reaction = 28,247 cal.

From Tables II and III, ΔS_{298} for the reaction = 29.5 E.U.

Calculating in the usual way, we have

$$\Delta F_{298} = 19,457 \text{ cal. and } I = 15.12.$$

Hence the general free energy equation may be expressed as follows:—

$$\Delta F_T = 26,401 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 15.12T.$$

The temperature of neutral equilibrium, $T_0 = 685^\circ\text{C}$.



The heats of reaction are (Table I)

$$\Delta H_{298} = 26,676 \text{ cal. and } \Delta H_0 = 24,830 \text{ cal.}$$

From Tables II and III, $\Delta S_{298} = 27.7$ E.U.

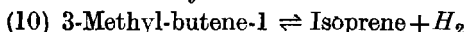
Employing the equations (X), (XI) and (VII), we have

$$\Delta F_{298} = 18,422 \text{ cal, } I = 16.91$$

and $\Delta F_T = 24,830 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 16.91T.$

The temperature of neutral equilibrium = 690°C .

Olefin isomers—Diolefins.



Equilibrium Data: Equilibrium constants for this reaction are given in Part IV. Assuming the specific heat equation (XI) and using the following two values of the equilibrium constants,

$$Kp = 0.00102 \text{ at } 643^\circ\text{K.}$$

$$Kp = 0.0111 \text{ at } 723^\circ\text{K.,}$$

we derive the following equation for heat of reaction:

$$\Delta H_T = 23,884 + 6.86T - 0.0023T^2 + 0.000,0002T^3.$$

Substituting $\Delta F_T = 6,465$ cal., at 723°K. , in equation (VII), we evaluate $I = 19.44$.

Hence, the standard free energy equation is:

$$\Delta F_T = 23,884 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 19.44T.$$

The validity of this free energy equation may be seen from the close agreement between the values of ΔF_T (Table VI) calculated directly from the equilibrium data and those obtained from the above equation.

TABLE VI.

No.	Temperature (absolute)	$\Delta F_T = -RT \ln Kp.$	ΔF°_T ; cal.
1	603	9,908	9,938
2	643	8,800	8,788
3	683	7,580	7,615
4	723	6,465	6,467

From the equations for the heat of reaction and free energy, we obtain

$$\Delta H_{298} = 25,750 \text{ cal.}, \Delta F_{298} = 18,228 \text{ cal.} \text{ and } \Delta S_{298} = 25.18 \text{ E.U.}$$

In order to derive the free energy equations for the dehydrogenation equilibrium of the two other isomers of 3-methyl-butene-1, it is now necessary to determine values of ΔH_{298} and ΔF_{298} for the formation of isoprene.

From Table I, 3-methyl-butene-1: $\Delta H_{298} = 6,578$ cal. and ΔH_{298} for the dehydrogenation process = 25,750 cal.

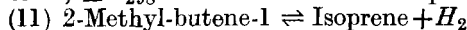
Therefore, ΔH_{298} for the formation of isoprene from the elements = 19,172 cal.

From the calorimetric and spectroscopic data:

3-Methyl-butene-1: $\Delta F_{298} = 18,062$ cal. and from the equilibrium data for the dehydrogenation reaction

$$\Delta F_{298} = 18,228 \text{ cal.}$$

Therefore, ΔF_{298} for the formation of isoprene = 36,290 cal.



From the data given in Table I, the heat of reaction is: $\Delta H_{298} = 27,596$ cal.

Assuming the specific heat equation (XI), we derive

$$\Delta H_T = 25,750 + 6.86T - 0.0023T^2 + 0.000,0002T^3.$$

Using, 2-Methyl-butene-1: $\Delta F_{298} = 16,216$ cal.

$$\text{Isoprene: } \Delta F_{298} = 36,290 \text{ cal.}$$

We calculate, $\Delta F_{298} = 20,074$ cal.

These data permit derivation of the following equation:

$$\Delta F_T = 25,750 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 19.37T.$$

and ΔS_{298} for the reaction = 25.2 E.U.



From the data on the heat of formation and free energy we calculate:

$$\Delta H_{298} = 29,167 \text{ cal.}, \Delta H_0 = 27,321 \text{ cal.},$$

$$\Delta F_{298} = 21,095 \text{ cal.}, \text{ and } \Delta S_{298} = 27.1 \text{ E.U.}$$

Making use of the above values, the following standard free energy equation is obtained:

$$\Delta F_T = 27,321 - 6.86T \ln T + 0.0023T^2 - 0.000,0001T^3 + 17.53T.$$

A summary of the more important derivations are given in the following table :—

Reactions.	Equations for standard free energies of the reactions	ΔH°_{298} cals.	ΔF°_{298} cals.	ΔS°_{298} E.U.	$T^\circ\text{C.}$
$n\text{-Butane} \rightleftharpoons \text{Butene-1} + H_2$	$\Delta F_T = 28,252 + x^* + 12.21T$	30,098	20,442	32.4	656
$n\text{-Butane} \rightleftharpoons \text{cis-butene-2} + H_2$	$\Delta F_T = 26,481 + x + 14.01T$	28,327	19,207	30.6	653
$n\text{-Butane} \rightleftharpoons \text{Trans-butene-2} + H_2$	$\Delta F_T = 25,531 + x + 14.6T$	27,377	18,437	30.0	640
$\text{Butene-1} \rightleftharpoons \text{Butadiene-1,3} + H_2$	$\Delta F_T = 25,496 + x + 20.03T$	27,342	20,015	24.6	744
$\text{Cis-butene-2} \rightleftharpoons \text{Butadiene-1,3} + H_2$	$\Delta F_T = 27,267 + x + 18.25T$	29,113	21,255	26.5	..
$\text{Trans-butene-2} \rightleftharpoons \text{Butadiene-1,3} + H_2$	$\Delta F_T = 28,259 + x + 17.5T$	30,105	22,025	27.1	..
$\text{Iso-pentane} \rightleftharpoons 3\text{-Methyl-butene-1} + H_2$	$\Delta F_T = 28,247 + x + 15.12T$	30,093	21,303	29.5	743
$\text{Iso-pentane} \rightleftharpoons 2\text{-Methyl-butene-1} + H_2$	$\Delta F_T = 26,401 + x + 15.12T$	28,247	19,457	29.5	685
$\text{Iso-pentane} \rightleftharpoons 2\text{-Methyl-butene-2} + H_2$	$\Delta F_T = 24,830 + x + 16.91T$	26,676	18,422	27.7	690
$3\text{-Methyl-butene-1} \rightleftharpoons \text{Isoprene} + H_2$	$\Delta F_T = 23,884 + x + 19.44T$	25,750	18,228	25.2	672
$2\text{-Methyl-butene-1} \rightleftharpoons \text{Isoprene} + H_2$	$\Delta F_T = 25,750 + x + 19.37T$	27,596	20,074	25.2	..
$2\text{-Methyl-butene-1} \rightleftharpoons \text{Isoprene} + H_2$	$\Delta F_T = 27,321 + x + 17.53T$	29,167	21,095	27.1	..

$$* x = -6.86T \ln T + 0.0023T^2 - 10^{-7}T^3$$

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