The significance of the condition that temperature and volume should be constant for thermodynamic description of interaction has been shown. A postulate concerning the potential energy of interaction $\varepsilon$ and the potential barrier $\varphi$ in relation to $\varepsilon$ has been obtained. These functions characterize directly the interaction in real thermodynamic systems. On this basis it has been possible to consider a wide range of problems and to obtain a number of new results (a general compensation effect for liquids and solutions, an equation for the critical point, etc.).

Interaction in real thermodynamic systems may be suitably investigated by using a special postulate concerning interaction side by side with the initial thermodynamics [1-5]. This consists of two assumptions, the first of which enables the determination of interaction to be carried out, and the second of which provides for the determination of a model system:

1. The energy of interaction is determined as the difference in the energies of the real and model system.
2. The model system without interaction for any degree of condensation satisfies the equation of state $PV = RT$.

This procedure leads to a number of very general results. We shall here consider some of these.

1. The Thermodynamic Description of Interaction. The Importance of the Conditions $T, V = \text{constant}$

The thermodynamic description of a process for particular conditions at which it is carried out (such as $T, P = \text{constant}$, or $S, V = \text{constant}$, etc.) consists of the determination of the change in internal energy $\Delta U$, of entropy $\Delta S$, and of other functions. All these conditions are of equal significance, but in each case the values $\Delta U, \Delta S$, etc., will generally speaking, take up different values, having different significance. The description of interaction within the framework of thermodynamics requires a strict delimitation of the conditions under which the process is carried out for the determination of this interaction.

We shall show that these limitations follow from the postulate that interaction occurs. The exclusion of interaction will be considered as a reverse transition of the real system $M$ into a system without interaction $M^*$:

$$ M \rightarrow M^*. $$  \hspace{1cm} (1)

The state $M^*$ is not yet completely determined, since it depends on the conditions of the process. We choose the conditions in such a way that the change in internal energy $\Delta U$ only takes into account the interaction effects. For this purpose it is necessary in the first place to exclude work done against the external pressure forces. This creates the condition $V = \text{constant}$. In the second place, in the limiting case (1), when $M$ also constitutes an ideal gas, $\Delta U$ should be equal to zero. Since the energy of an ideal gas depends on the temperature, this gives the second condition $T = \text{constant}$.

Thus, if we are concerned with the thermodynamic description of interaction, the conditions $T, V = \text{constant}$ represent those to be selected from amongst all other possible conditions.

The change in internal energy $\Delta U_{T,V}$ is made up of two terms:

$$ \Delta U_{T,V} = \Delta F_{T,V} + T\Delta S_{T,V}. $$  \hspace{1cm} (2)

The free energy difference $\Delta F = F^* - F$ is equal to the work eliminating interaction. Here we take account of the extrapolation of the concept of mechanical potential energy in the case of systems whose properties depend on the temperature. The term $T\Delta S$ represents the heat of the process, or, in other words, the energy which the system eliminating interaction takes spontaneously from the thermostat. We shall introduce the notations:

$$ E = \Delta U_{T,V}, \quad \varepsilon = \Delta F_{T,V}. $$  \hspace{1cm} (3)

The values of $\varepsilon$ and $E - \varepsilon$, as in the case of $E$ itself, are functions of the state of the real system. We observe that other additional functions of state may exist (internal work and internal heat) as already indicated by Clausius [6] and Planck [7]. These have not, however, proved capable of separation.

2. The Functions $E, \varepsilon$, and $E - \varepsilon$ in a Wide Temperature Range

An ideal gas constitutes a system with the maximum disorder, and therefore with the maximum entropy in comparison with any other state in which interaction occurs. Hence $(S^* - S)_T, V > 0$, and consequently $\varepsilon < E$. This obvious
inequality is true for all real systems. Numerical calculations [3] show that for liquids of different structure in a wide
temperature range, the ratio \( \varepsilon/E \) lies as a rule within the limits 0.4—0.6, and is on the average 0.5. Similar data were
obtained for crystalline bodies at the melting point (Table 1).

<table>
<thead>
<tr>
<th>( \varepsilon/E )</th>
<th>( \varepsilon )</th>
<th>H(_2\O)</th>
<th>n-C(<em>6)H(</em>{14})</th>
<th>C(_6)H(_6)</th>
<th>cyclo-C(_8)H(_8)</th>
<th>NH(_3)</th>
<th>C(_2)H(_2)</th>
<th>CO(_2)</th>
<th>Ar</th>
<th>N(_2)</th>
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<tr>
<td>kcal/mole</td>
<td>kcal/mole</td>
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</tr>
<tr>
<td>6.1</td>
<td>0.52</td>
<td>5.36</td>
<td>4.37</td>
<td>4.07</td>
<td>3.26</td>
<td>1.78</td>
<td>1.59</td>
<td>0.81</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Values of \( \varepsilon/E \) for Crystalline at the Melting Point

To eliminate interaction when \( T, V = \) constant, e.g., in crystalline argon, it is necessary to use an energy \( E = 1.69 \)
kcal/mole. Part of this energy, \( \varepsilon = 0.81 \) kcal/mole, must be supplied in the form of work, while the remaining energy,
\( 1.69-0.81 = 0.88 \) kcal/mole is supplied spontaneously in the form of heat from the thermostat. The result is that the
total energy of interaction is divided equally between the potential and entropy components:

\[
\varepsilon = E - \varepsilon = 0.5E. \tag{4}
\]

We observe that the heat of the process cannot be determined from the difference in the translational energy per
mole of vapor and the kinetic vibrational energy of the molecule in the crystal. Such a calculation for argon at the
melting point gives \( 3/2 RT - 3/2 RT = 0 \), while \( E - \varepsilon = 0.88 \) kcal/mole.

With reduction in temperature the ratio \( \varepsilon/E \) increases, and in the limit

\[
\varepsilon \rightarrow E \text{ when } T \rightarrow 0. \tag{5}
\]

This limiting relationship is easy to show by using the Clausius-Clapeyron equation, and the fact that the pressure of the
saturated vapor over the crystal approaches zero as the absolute temperature approaches zero. On the other hand, the rela-
tionship (5) follows from the fact that \( T \Delta S_{T,V} \rightarrow 0 \) since \( T \rightarrow 0 \) (\( \Delta S_{T,V} \neq 0 \)). From this we obtain the natural limit for the incre-
ase in \( \varepsilon \) with reduction in temperature. Figure 1 shows the results of calculating \( \varepsilon/E \) at low temperature for
solid water and carbon dioxide, and also for liquid helium at a temperature greater than 2,186 K. The dependence of
the ratio \( \varepsilon/E \) on \( T \) is practically linear, and within the limits of accuracy of the calculation leads to \( \varepsilon/E = 1 \), when
\( T = 0 \).

Fig. 1. Dependence of \( \varepsilon/E \) on temperature for solid water and carbon dioxide and for liquid helium-1 (without taking into account
degeneration effects of the ideal gas).

Fig. 2. The reaction \( \text{H}_2 \rightarrow 2\text{H} \) as an exclusion of interaction. The interaction function is given
in a wide range of temperature. Calculation is from data in [8].

We also use the postulate of interaction without any limitation for chemical reactions. As an example we will con-
sider the simplest reaction \( \text{H}_2 \rightarrow 2\text{H} \) as an exclusion of interaction. We shall suppose that \( \text{H}_2 \) represents the condition in
which the interaction occurs, while \( \text{H} \) is the condition without interaction. The values of \( E, \varepsilon, \) and \( E - \varepsilon \), in the tem-
perature range from 0 to 4000 K are shown in Fig. 2. The total interaction \( E \) in this range only slightly changes, while
the potential \( \varepsilon \) and entropy \( E - \varepsilon \) components change almost according to a linear law in opposite directions to each