Monatshefte für Chemie 127, 1247–1249 (1996)

**Monatshefte für Chemie**
**Chemical Monthly**


## *Short Communication*

# Dependence of the Internal Energy on the Temperature During Chemical Reactions

**I. A. Stepanov**

Juglas 1a/20, Riga-24, Latvia

**Summary.** Using results obtained earlier it has been shown that the internal energy varies during chemical reactions with the temperature according to $U = U_0 + f(T) + DT$ for the reactants and $U = U'_0 + f(T) + D'T$ for the products.

**Keywords.** Kinetics; Energy of activation; Internal energy.

**Abhängigkeit der inneren Energie von der Temperatur bei chemischen Reaktionen (Kurze Mitt.)**

**Zusammenfassung.** Unter Verwendung früher erhaltener Ergebnisse konnte gezeigt werden, daß die innere Energie bei chemischen Reaktionen nach $U = U_0 + f(T) + DT$ (Reaktanden) bzw. $U' = U_0 + f(T) + D'T$ (Produkte) von der Temperatur abhängt.

## Introduction

In Refs. [1, 2] it has been shown that the *Arrhenius* equation has the form

$$k = Z\exp(-(E_0 + BT)/RT)$$

where $k$ is the reaction rate constant, $Z$ is the number of molecular collisions, $E_0 + BT$ is the energy of activation, and $B$ is the proportionality coefficient. Thus, the energy of activation depends linearly on the temperature. In the present investigation, this result is applied to the analysis of the dependence of the internal energy on the temperature during chemical reactions.

## Methods

The energy of activation of a chemical reaction can be written as

$$E_a = E^{\#} - U$$

where $E^{\#}$ is the energy of the transition state and $U$ is the sum of the internal energies of the chemical reactants. The energy of the activation of the inverse reaction is equal to

$$E'_a = E^{\#} - U'$$

where $U'$ is the sum of the internal energies of the products of reaction. Hence

$$E'_a - E_a = U - U'.$$

According to Refs. [1, 2],

$$E_a = E_0 + BT$$

and

$$E'_a = E'_0 + B'T.$$

Therefore,

$$E'_0 + B'T - E_0 - BT = U - U' \tag{1}$$

$$U = U_0 + \Delta U \tag{2}$$

$$U' = U'_0 + \Delta U' \tag{3}$$

where $U_0$, $U'_0$ are the sums of the internal energies of the chemical reactants and of the products at 0 K, respectively, and $\Delta U$, $\Delta U'$ is the increase in energy.

Substituting Eqs. (2) and (3) in Eq. (1), we obtain

$$E'_0 - E_0 + B'T - BT = U_0 - U'_0 + \Delta U - \Delta U'.$$

When $T = 0$,

$$E'_0 - E_0 = U_0 - U'_0.$$

Hence,

$$B'T - BT = \Delta U - \Delta U'.$$

## Results and Discussion

We see that in chemical reactions the internal energy of reactants and products varies with the temperature according to

$$U = U_0 + f(T) + DT \tag{4}$$

and

$$U' = U'_0 + f(T) + D'T, \tag{5}$$

where $f(T)$ is a function of temperature and $D$ and $D'$ are constants. $f(T)$ is the same both for reactants and products, $D - D' = B' - B$.

This is an interesting result, since it contradicts all theories known before. It is a simple consequence of the experimentally found fact that $E_a = E_0 + BT$ can explain many paradoxes in kinetics [1].

It should be noticed that earlier it was thought that the internal energy of a substance is its whole energy. In Ref. [3] it was deduced that the internal energy is only the thermal energy of motion of molecules. This is a contradiction to the postulate in thermodynamics that the internal energy is the whole energy. Assuming that internal energy is only the thermal energy of motion of molecules solves the paradoxon in Ref. [3]. If this assumption holds, then $U_0$, $U'_0 \rightarrow 0$ for $T \rightarrow 0$, and Eqs. (4) and (5) turn to

$$U = f(T) + DT$$

and

$$U' = f(T) + D'T.$$

## References

[1] Stepanov IA (1993) Journ Therm Anal **39**: 1375
[2] Stepanov IA (1994) Fire and Explosion Safety **1**: 3
[3] Stepanov IA, DEP VINITI No 37-B96, 03.01. 1996 (Moscow)

*Received July 8, 1996. Accepted (revised) September 4, 1996*