

## On the Theory of Non-Isothermal Systems

HANS HOLTAN JR.\*

Recently the thermodynamics of irreversible processes<sup>1</sup> has been applied to thermocells<sup>2-4</sup>. For the homogeneous potential difference the following expression was obtained

$$F \text{ grad } \varphi = - \sum_{K=1}^n (t_K/z_K) (\text{grad } \mu_K)_{P,T} - \sum_{K=1}^n (t_K/z_K) Q_K^* (\text{grad } T)/T \quad (1)$$

where  $F$  is Faraday's number,  $\varphi$  the electric potential,  $t_k$  and  $z_k$  the transference number and charge of component  $k$  respectively;  $\mu_k$  is the chemical potential of component  $k$  expressed in mole units, and  $Q_k^*$  is the molar heat of transfer of component  $k$ , *i. e.* the heat transported with one mole of component  $k$  at uniform temperature, and  $T$  is the absolute temperature.

An expression quite analogous with (1) may easily be derived by means of the *principle of thermal interaction* which originally was introduced by the author<sup>5</sup> as an alternative to the Eastman-Wagner<sup>6,7</sup> theory. In the language of Brønsted's energetics<sup>8,9</sup> the principle states that a "loss of work" connected to the movement of matter may be compensated partly or completely by the transport of free entropy in the opposite direction.

Consider a transport of one mole of component  $k$  from a region of a conductor of temperature  $T$ , pressure  $P$ , electric potential  $\varphi$  and chemical potential  $\mu$  to a region of temperature  $T + dT$ , pressure  $P + dP$ , electric potential  $\varphi + d\varphi$  and chemical potential  $\mu_k + d\mu_k$ . Such a transport is accompanied by the "loss of work" (loss of potential energy):

$$\sum \partial A = - S_k dT - z_k F d\varphi + V_k dP - d\mu_k + S_k''' dT \quad (2)$$

where  $\Sigma A$  is the total "loss of work",  $S_k$  and  $V_k$  are the transported entropy and volume respectively and  $S_k'''$  the compensated entropy of component  $k$ . The term  $S_k''' dT$  takes care of the interaction between the flow of matter and the flow of heat which takes place at all times in a system where temperature gradients are present.

In the stationary state

$$\sum \partial A = 0. \quad (3)$$

\* Present address: Det Norske Zinkkompani A/S, Odda, Norway.

As we have

$$d\mu_K = (d\mu_K)_{P,T} + V_K dP - S_K dT \quad (4)$$

we obtain from (2) the following equation in the stationary state when multiplying both sides of the equation with  $t_k$  and summing from  $k = 1$  to  $k = n$ :

$$F d\varphi = - \sum_{K=1}^n \frac{t_K}{z_K} (d\mu_K)_{P,T} + \sum_{K=1}^n \frac{t_K}{z_K} S_K''' dT \quad (5)$$

We see that (5) is quite analogous with (1) and comparison shows that

$$S_K''' = -Q_K^*/T \quad (6)$$

As the expressions for the heterogeneous potential differences contain no interaction terms, the expression for the total thermopotential difference will also be quite analogous according to both methods. As shown by the author<sup>2</sup> this expression reads in cases where there are no concentration gradients:

$$F \Delta\varphi_t = - \sum_{K=1}^n (t_K/z_K) Q_K^* \Delta T/T - (Q_{el}^*/T) \Delta T - \Delta S \Delta T \quad (7)$$

where  $\Delta\varphi_t$  is the resultant potential difference,  $Q_{el}^*$  and  $S_{el}$  the molar heat of transfer and the molar entropy of the electrons in the metallic part of the cell respectively, and  $\Delta S$  the change of entropy accompanying the heterogeneous electrode reaction when one Faraday of electricity passes the interface.

The same expression is of course obtained by means of the principle of thermal interaction except for the fact that  $Q_{el}^*$  should be replaced by  $-S_{el}''' T$ , and  $Q_k^*$  by  $-S_k''' T$  according to (6).

As shown by the author<sup>2</sup> it is of advantage to split up the expression (7) in the following way.

$$F \Delta\varphi_t = - \sum_{K=1}^n (t_K/z_K) (Q_K^* + T S_K)/T - (Q_{el}^* + T S_{el})/T - \Delta S + \sum_{K=1}^n (t_K/z_K) S_K + S_{el} \quad (8)$$

The first part (the two first terms on the right hand side) contains heats of transfer, which are kinetic quantities, while the second part (the three last terms on the right-hand side) consists of well known quantities.

A number of calculations of the second part have been performed by the author<sup>2</sup>. It is remarkable that for thermocells with solid electrolyte the calculated values agree with the experimental ones<sup>10-12</sup>, which means that the first part of the thermocell expression is negligible in these cases.

Considering (8) we see that the first term on the right hand side disappears if

$$Q_K^* = -T S_K \quad (9)$$

or if, cf. (6)

$$S_k''' = S_k \quad (10)$$

Therefore, if the compensated entropy of component  $k$  is equal to the total entropy of component  $k$  ("full compensation"), the first term vanishes.

As the second term is small in any case (the thermopotentials in metallic thermocouples are of a smaller order of magnitude than in electrolytic cells), the first part will practically vanish when (9) or (10) are fulfilled, and the expression for the thermopotential becomes purely thermostatic. This thermostatic expression for the potential in thermocells with solid electrolyte has formerly been derived by the author<sup>5</sup> by means of the principle of thermal interaction by introducing (10) from the beginning. This procedure is not quite logical and it had been better to derive the general expression for the thermopotential difference first, as has been done here. From the fact that calculations of the thermostatic part of the potential difference for thermocells with solid electrolyte show agreement with experimental results, one should be careful not to conclude that the compensation is complete also in other cases, or in other words that stationary states in general can be described by means of thermostatic variables alone. This fact has been stressed by Mazur<sup>13</sup>.

The compensated entropy is in fact a kinetic quantity and it is a good approximation to replace it by the thermostatic entropy only in special cases, and the introduction of the compensated entropy in relation (2) is in reality analogous with the way of expressing the interaction by means of phenomenological relations as done in the general theory of irreversible processes<sup>1</sup>. The basis of this theory is formed by the Onsager relations, which permit a coupling of phenomena occurring in quite different situations. For instance the heat of transfer appearing in the expressions for the electrical potential differences in *non-isothermal* systems is given as the heat transported with the unit mass at *uniform temperature*, *i. e.* in a quite different situation.

The derivation of the homogeneous thermopotential difference is extremely simple when the principle of thermal interaction is applied. One arrives directly at expression (5) without the application of Onsager's relations of reciprocity. However, if we want to derive for instance relation (6) or the second Thomson relation we must of course apply the Onsager relations as is done in the general theory of irreversible processes. It is, however, not always necessary to compare with different situations, and the kinetic quantity, the compensated entropy may as well be calculated directly from kinetic theories as the related quantity, the heat of transfer, given in a different physical situation. The principle of thermal interaction is lacking in generality as it of course only applies to phenomena in non-isothermal systems, but it is probably possible to generalize the principle to include a wider range of phenomena.

It is of interest to consider the value of the compensated entropy in some extreme cases.

Consider first a uncharged gaseous system contained in two containers separated by a tube. The two containers are supposed to have the same volume, but the temperatures differ by  $dT$  and the pressures by  $dP$ , respectively.

Since no net volume is transported equation (2) reads in this case for a transport of one mole of substance between the two containers<sup>14</sup>

$$\sum \delta A = -S_K dT - d\mu_K + S_K'' dT \quad (11)$$

We then get in the stationary state (cf. (3))

$$dP/dT = S_K'''/V_K \quad (12)$$

If the separation tube is very narrow (of dimensions comparable with the mean free path of the molecules of the gas) and the pressure low, we find by comparison with the Knudsen equation that

$$S_K''' = R/2 \quad (13)$$

We see that the energy of compensation  $S_K''' T$  equals  $RT/2$ , which means that only one degree of translational motion is compensated for; a quite reasonable result for a substance where there are no forces acting between the particles. As shown by de Groot<sup>1</sup> the heat of transfer for this case can easily be derived from the kinetic gas theory.

If there were forces acting between the particles of the gas passing between the two containers, one expects a larger value for the compensated entropy.

Consider then another extreme case, *viz.* thermocells with solid salts. We have seen that the compensation is complete in this case. Thus, in this case where the particles are bound to their places by rather strong forces, practically all their entropy is compensated for.

For intermediate cases we will expect values of  $S_K'''$  between  $R/2$  and  $S_K$ , and therefore, for instance for thermocells with electrolytic solutions, the kinetic part of the thermopotential should not be of negligible magnitude, and the expression for the Soret effect in solutions should also be expected to contain a kinetic term, *i. e.* it can not be expressed in terms of thermostatic variables alone. A calculation of the compensated entropy or the heat of transfer in these cases must be based on a kinetic treatment taking the structure, the forces and the degrees of freedom into account.

The splitting up of the general thermocell equation as performed by the author<sup>2</sup> in applying the general theory of irreversible processes to thermocells is rather artificial and the result found that the kinetic part of the expression is of negligible magnitude when the electrolyte is a solid salt is surprising from this point of view. The result is more logical from the point of view of the principle of thermal interaction, and the author was actually lead to this splitting up of the thermopotential difference expression from his previous knowledge of the principle of thermal interaction.

Krogh-Moe<sup>15</sup> has recently indicated that the principle of thermal interaction is embodied in the principle of least dissipation of energy<sup>16</sup>.

#### SUMMARY

The expression for the thermopotential difference in non-isothermal cells (thermocells) can be derived simply and logically by means of the principle of thermal interaction, and the results obtained have been shown to be consistent with those obtained by applying the general (but for this purpose more complicated) theory of irreversible processes.

A discussion of the two quantities, heat of transfer and compensated entropy has been put forward. The latter quantity is in reality introduced in a way analogous to the introduction of phenomenological relations in the thermodynamical theory of irreversible processes, and this fact explains why the two methods lead to consistent results.

## REFERENCES

1. de Groot, S. R. *Thermodynamics of Irreversible Processes*, North Holland Publ. Company, Amsterdam, and Intersc. Publ., New York, 1951.
2. Holtan, H., Jr. *Electric Potentials in Thermocouples and Thermocells*, Thesis, Utrecht 1953.
3. Holtan, H., Jr., Mazur, P. and de Groot, S. R. *Physica* **19** (1953) 1109.
4. Holtan, H., Jr. *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B* **56** (1953) 498; **56** (1953) 510.
5. Holtan, H., Jr. *J. Chem. Phys.* **19** (1951) 519.
6. Eastman, E. D. *J. Am. Chem. Soc.* **48** (1926) 1482; **49** (1927) 794; **50** (1928) 292.
7. Wagner, C. *Ann. Phys.* [5] **3** (1930) 629; **6** (1930) 370.
8. Holtan, H., Jr. *Tidsskr. Kjemi, Bergvesen. Met.* **8** (1948) 124.
9. Holtan, H., Jr. *Tek. Ukeblad* **95** (1948) 624.
10. Reinhold, H. *Z. anorg. Chem.* **171** (1928) 181.
11. Reinhold, H. *Z. phys. Chem. B* **11** (1931) 321.
12. Holtan, H., Jr. *Tidsskr. Kjemi, Bergvesen. Met.* **12** (1952) 5.
13. Mazur, P. *J. Chem. Phys.* **19** (1951) 1431.
14. Brønsted, J. N. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **15** (1937) No. 4.
15. Krogh-Moe, J. *Acta Chem. Scand.* **7** (1953) 239.
16. Wergeland, H. *Kgl. Norske Videnskab. Selskabs Forh.* **24** (1951) No. 25.

Received June 23, 1953.