The Onsager symmetry relations play a pivotal role in the investigation of nonquilibrium processes. The present worksheet is devoted to some of their properties.

**Exercise 10: Onsager and state of minimal entropy production**

We consider a composite system made of two parts 1 and 2. The latter have two different temperatures $T_1$ and $T_2$, and can exchange energy and matter. Show that the entropy production in the stationary state has a minimum as a function of the affinities when the Onsager relations are satisfied.

**Exercise 11: Onsager and response in an electrical network**

A passive electrical network has two pairs of terminals, the d.c. voltage and current at one pair being $V_1, I_1$ and $V_2, I_2$ at the other. These are related by the equations,

$$I_1 = L_{11} V_1 + L_{12} V_2 ,$$
$$I_2 = L_{21} V_1 + L_{22} V_2 .$$

(1)

The network is assumed to be of such a nature that the determinant of the coefficients is non-zero: this means that $I_1$ and $I_2$ cannot both be zero unless $V_1$ and $V_2$ both vanish. Obtain the Onsager relation for the coefficients in these equations by the following steps.

a) Suppose the capacitances $C_1$ and $C_2$ are connected across the two pairs of terminals. Denote the charges on these capacitances by $q_1$ and $q_2$. Show that if the whole system is at temperature $T$, then,

$$\langle \Delta X^2 \rangle = k_B T \left( \frac{\partial \langle X \rangle}{\partial F} \right)_T .$$

b) Express the equations giving $I_1, I_2$ in terms of $V_1, V_2$ as equations relating $\dot{q}_1, \dot{q}_2$ to $q_1, q_2$.

c) Use the time reversal result,

$$\langle q_1 \dot{q}_2 \rangle = \langle \dot{q}_1 q_2 \rangle .$$

to derive the Onsager relations.

**Exercise 12: Paper-Work**

Find the following article online and answer the following questions:

- What is the paper about?
• Why is it interesting?
• What is done?
• How is it done?

Thermodynamics of irreversible processes
D. Miller, Chem. Rev. 60, 15 (1960) – Sections I to IV.

The Origins of Onsager’s Key Role in the Development of Linear Irreversible Thermodynamics