Lösungen zum Übungsblatt 10

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Problem 1: Thermodynamic Relations and Clausius-Clapeyron equation:

Tasks:

a) Show the following thermodynamic relation:

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p \tag{1}$$

b) Show the following thermodynamic relation:

$$\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T + \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p^2 \tag{2}$$

Methods:

a) We'll show the Maxwell-relation (*proof 1*):

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{3}$$

and after a few transformations we'll insert it in the definition of the spesific heat by a constant pressure:

$$C_p := T\left(\frac{\partial S}{\partial T}\right)_p \tag{4}$$

b) We concider the functions $f(u,v)$ and $g(u,v)$ and want to prove the following assertions:

2) The Jacobians can be simplified as followed

$$\frac{\partial(f,g)}{\partial(u,g)} = \left(\frac{\partial f}{\partial u}\right)_g \qquad \frac{\partial(f,g)}{\partial(f,v)} = \left(\frac{\partial g}{\partial v}\right)_f \tag{5}$$

3)

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{6}$$

4)

$$\left(\frac{\partial f}{\partial u}\right)_v = -\frac{\left(\frac{\partial f}{\partial v}\right)_u}{\left(\frac{\partial u}{\partial v}\right)_f} \tag{7}$$

5)

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S} \tag{8}$$

Results:

Appendix:

a) If we multiply (4) with ∂V we obtain:

$$\partial V C_p = T \partial V \left(\frac{\partial S}{\partial T}\right)_p$$
$$\Rightarrow \left(\frac{\partial V}{\partial S}\right)_p = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p$$

With the Maxwell-relation (3) prooved in *proof 1* we obtain our relation (1):

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p$$

proof 1: We start with the differential of the enthalpy $H(S,p)$:

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p$$

with the obvios equations:

$$T = \left(\frac{\partial H}{\partial S}\right)_p \qquad V = \left(\frac{\partial H}{\partial p}\right)_S$$

Now we use the permutability of differentations:

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\partial^2 H}{\partial p\,\partial S} = \frac{\partial^2 H}{\partial S\,\partial p} = \left(\frac{\partial V}{\partial S}\right)_p \quad \square$$

b) We start with the definition of the specific heat by a constant temperature and use the relations (5):

$$\begin{aligned}
C_V := T\left(\frac{\partial S}{\partial T}\right)_V &= T\cdot\frac{\partial(S,V)}{\partial(T,V)} \\
&= T\cdot\frac{\partial(S,V)}{\partial(T,p)}\frac{\partial(T,p)}{\partial(T,V)} \\
&= T\left(\frac{\partial p}{\partial V}\right)_T\frac{\partial(S,V)}{\partial(T,p)} \\
&= T\left(\frac{\partial p}{\partial V}\right)_T\left[\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T-\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\right] \\
&= T\left(\frac{\partial S}{\partial T}\right)_p-T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p
\end{aligned}$$

With the Maxwell-relation (6), $\alpha := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and the definition of the isothermal compressibility $\kappa_T := -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ we obtain:

$$C_V = C_p + T\frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T}$$

$$\Rightarrow C_p - C_V = \frac{T\alpha^2}{\kappa_T}$$

With (8) we obtain:

$$\kappa_S = \kappa_T - \frac{TV\alpha^2}{C_p}$$

$$\Rightarrow -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T - \frac{TV\left(\frac{\partial V}{\partial T}\right)_p^2}{V^2C_p}$$

$$\Rightarrow \left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T + \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p^2$$

proof 2: We also concider the functions $f(u,v)$ and $g(u,v)$. The Jacobian is defined by:

$$\frac{\partial(f,g)}{\partial(u,v)} = \left(\frac{\partial f}{\partial u}\right)_v\left(\frac{\partial g}{\partial v}\right)_u - \left(\frac{\partial f}{\partial v}\right)_u\left(\frac{\partial g}{\partial u}\right)_v$$

Now we set $g = v$. $\left(\frac{\partial v}{\partial u}\right)_v = 0$ and $\left(\frac{\partial g}{\partial v}\right)_u = 1$ is trivial and we obtain:

$$\frac{\partial(f,v)}{\partial(u,v)} = \left(\frac{\partial f}{\partial u}\right)_v$$

With the same argumentation you can find with $f = u$:

$$\frac{\partial(u,g)}{\partial(u,v)} = \left(\frac{\partial g}{\partial v}\right)_u \qquad \square$$

proof 3: We concider the potential of the free enthalpy $G(T,p)$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$$

and find the relations:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \qquad\qquad V = \left(\frac{\partial G}{\partial p}\right)_T$$

With the same argumentation as in *proof 1* we obtain the Maxwell-relation:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial V}{\partial T}\right)_p \qquad \square$$

proof 4: With the use of *proof 2* we obtain:

$$\left(\frac{\partial f}{\partial u}\right)_v = \frac{\partial(f,v)}{\partial(u,v)} = \frac{\partial(f,v)}{\partial(f,u)}\frac{\partial(f,u)}{\partial(u,v)} = -\frac{\left(\frac{\partial f}{\partial v}\right)_u}{\left(\frac{\partial u}{\partial v}\right)_f} \qquad \square$$

proof 5: We start with the entropy $S(V,T)$ and (7):

$$\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial T}{\partial V}\right)_S \cdot \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial T}{\partial V}\right)_S} \\
&= -\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V \\
\Rightarrow -\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T &= \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V \\
\Rightarrow -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial T}{\partial p}\right)_S} \left(\frac{\partial p}{\partial V}\right)_T &= \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial S}{\partial T}\right)_V \\
\Rightarrow \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V \\
\Rightarrow -\frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial V}{\partial p}\right)_S &= -\frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T
\end{aligned}$$

With the definitions of the specific heat and the compressibility we obtain:

$$C_p \kappa_S = C_V \kappa_T \qquad \square$$

Problem 2: Solar Cells and Geothermal Energy

(a) The solar constant specifies the average energy, that reaches the surface of the earth averaged per square meter per second, is $1.367\text{kJm}^{-2}\text{s}^{-1}$. Since about one third of the arriving energy is reflected, only $I = 0.96\text{kJm}^{-2}\text{s}^{-1} \approx 1\text{kJm}^{-2}\text{s}^{-1}$ actually reach the surface.

Knowing that the radiation's temperature is $T_2 = 6000\text{K}$ and estimating $T_1 = 290\text{K}$ on earth, we obtain the Carnot efficiency:

$$\eta_{\text{C}} = \frac{T_2 - T_1}{T_2} = 0.95 \quad .$$

This means that the maximum power P_{max}, a 1m^2 solar cell can obtain hypothetically, is

$$P_{\text{max}} = \eta_{\text{C}} I \cdot 1\text{m}^2 = 0.91\text{kJs}^{-1} = 910\text{W} \quad .$$

This calculation ignores, that the solar cell's temperature probably will increase to higher values than 290K.

(b) We assume a real efficiency $\eta_{\text{r}} = 0.05$ of a solar cell. This leads to:

$$P_{\text{r}} = \eta_{\text{r}} I \cdot 1\text{m}^2 = 48\text{W} \quad .$$

We regard a cell, that does its job for 30 years, 5 hours a day. The "produced" electrical energy during this time is

$$E = \underbrace{30 \cdot 365 \cdot 5 \cdot 60 \cdot 60}_{=:\ t\ [\text{s}]} \cdot 48\text{W} = 9461 \cdot 10^6\text{J} = 2628\text{kWh} \quad ,$$

since $[\text{kWh}] = 1000 \cdot [\text{W}] \cdot 60^2$.

We can compute the adequate price p of the solar cell as follows, assuming 0.15\$/kWh:

$$p = 2628\text{kWh} \cdot 0.15\$/\text{kWh} = 394.2\$ \quad .$$

After 30 years, the solar cell is profitable.

(c) With

$$\text{d}Q = c \cdot \text{d}T \quad ,$$

where $c = 1000\text{Jkg}^{-1}\text{K}^{-1} \cdot 10^{14}\text{kg}$ is the specific heat of the rock, we get the change of energy during a change of temperature. To compute the energy $\text{d}W$, the power plant "produces", we need its efficiency.

Similar to task (a), the efficiency is computed by:

$$\eta_{\text{C}} = \eta_{\text{C}}(T) = \frac{T - T_W}{T} \qquad (T_W = 20°C = 293\text{K}) \quad ,$$

with the difference, that one of both temperatures (T) is not a constant.

Now we get:

$$\mathrm{d}W \ = c \cdot \eta_{\mathrm{C}}(T)\, \mathrm{d}T \quad .$$

The total amount of energy is:

$$\begin{aligned}
W = \int \mathrm{d}W \ &= c \cdot \int\limits_{T_i}^{T_f} \eta_{\mathrm{C}}(T)\, \mathrm{d}T \\
&= c \cdot \int\limits_{T_i}^{T_f} \frac{T - T_W}{T}\, \mathrm{d}T \ = c \cdot \int\limits_{T_i}^{T_f} \left(1 - \frac{T_W}{T}\right) \mathrm{d}T \\
&= c \cdot \left[T - T_W \cdot \ln T\right]_{T_i}^{T_f} \\
&= c \cdot (T_f - T_W \cdot \ln T_f - T_i + T_W \cdot \ln T_i) \\
&= -2.49 \cdot 10^{19}\ \mathrm{J} \\
&= -6.91 \cdot 10^{12}\ \mathrm{kWh} \quad ,
\end{aligned}$$

with $T_i = 600°C = 873K$ and $T_f = 110°C = 383K$. The negative value indicates, that the energy leaves the system (the power plant).