Exercises on Ch.1 *Basic concepts of thermodynamics*

1.1 External state variables. Exercise 1

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1.1 *External state variables*

Exercise 1.1.1

A system consists of two subsystems with the values U_1, V_1, P_1 and U_2, V_2, P_2, where U is the internal energy. U and V are both extensive quantities. The law of additivity applies to them and we have for the complete system $U = U_1 + U_2$; $V = V_1 + V_2$. One often defines another function, enthalpy $H = U + PV$, where P is the external pressure. Evidently, H is also a state function and an extensive quantity. Discuss whether the law of additivity applies to H in a way that $H = U_1 + P_1V_1 + U_2 + P_2V_2$.

Hint

Before we discuss this question, it is necessary to define the situation better. How can the two different pressures be maintained? You may find two different cases.

Solution

In principle, one can change any one of V_1, V_2, U_1 and U_2 by making the opposite change in the surroundings. For the surroundings we get a change in volume of $-\mathrm{d}V = -\mathrm{d}V_1 - \mathrm{d}V_2$ and in energy of $-\mathrm{d}U = -\mathrm{d}U_1 = \mathrm{d}U_2$ and V and U are state variables of the complete system. For pressure there are two possibilities. One possibility is that the subsystems have direct contact with two different surroundings of pressures, P_1 and P_2. We may then accept that H is additive but actually we have to derive a whole new set of thermodynamic equations using two external pressures. Another possibility is that one subsystem (1) is enclosed in the other (2) and the surface tension of the interface gives the pressure difference $P_1 - P_2 = 2\sigma/r$. In the calculation of the total enthalpy of the system one must also include the surface energy of the interface U_{int}: $H = U + P_2V = U_1 + U_2 + U_{\text{int}} + P_2(V_1 + V_2) = U_1 + P_2V_1 + U_2 + P_2V_2 + U_{\text{int}}$. One will thus obtain $H = H_1 + H_2 + U_{\text{int}}$ if one defines $H_1 = U_1 + P_2V_1$ instead of $H_1 = U_1 + P_1V_1$, which may be justified because P_2 represents an external variable but P_1 is an internal variable that cannot be controlled from the outside.

1.3 *The first law of thermodynamics*

Exercise 1.3.1

Consider a system under such conditions that there is no exchange of heat or work with the surroundings. Suppose there is some spontaneous reaction inside the system. What can we say about the change of the internal energy?

Solution

It follows directly from the definition that U does not change, $\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = 0 + 0 = 0$.

Exercise 1.3.2

Consider a system at T_1,P_1,V_1, which is composed of one mole of a ideal classical gas for which $PV = RT$ and $U = A + BT$. Let the system change in four steps. The first step is a very slow compression to P_2, V_2 at a constant temperature of T_1. The second step is a very quick compression to T_3,P_3,V_3. The third step is a very slow expansion to P_4, V_4 at a constant temperature of T_3. The fourth step is a very quick expansion back to T_1,P_1,V_1. The second and fourth steps are so quick that there is no heat exchange. Calculate the relations between the total work done by the system, the absorbed heat of the first step and the heat of the third step, expressing the result in terms of T_1 and T_3.

Hint

$\Sigma\Delta U = 0$ because the system returns to the initial state. Thus, $Q_1 + Q_3 + W_1 + W_2 + W_3 + W_4 = 0$. Furthermore, U is only a function of T and thus $\Delta_1 U = 0$ and $\Delta_3 U = 0$ giving $Q_1 + W_1 = 0$ and $Q_3 + W_3 = 0$ and thus $W_2 + W_4 = 0$. Consequently, the net work done on the system $W = W_1 + W_3$. The problem is to calculate W_1 ($= -Q_1$) and W_3 ($= -Q_3$) and to relate them using T_1 and T_3.

Solution

$W_1 = -\int P\mathrm{d}V = -RT_1\int \mathrm{d}V/V = -RT_1\ln(V_2/V_1)$; $W_3 = -RT_3\ln(V_4/V_3)$. The second step where $Q_2 = 0$ gives $\mathrm{d}U = \mathrm{d}W$; $B\mathrm{d}T = -P\mathrm{d}V = -RT\mathrm{d}V/V$; $B\ln(T_3/T_1) = -R\ln(V_3/V_2)$ and the fourth step $B\ln(T_1/T_3) = -R\ln(V_1/V_4)$. Thus $V_3/V_2 = V_4/V_1$ or $V_1/V_2 = V_4/V_3$ and $W_1/T_1 = R\ln(V_1/V_2) = R\ln(V_4/V_3) = -W_3/T_3$. The work done by the system is $-W = -W_1 - W_3 = -W_1 + W_1T_3/T_1 = W_1(T_3 - T_1)/T_1 = -W_3(T_3 - T_1)/T_3 = -Q_1(T_3 - T_1)T_1 = Q_3(T_3 - T_1)/T_3$. By drawing the heat Q_3 from a heat source at T_3 one may thus produce mechanical work in the amount of $Q_3(T_3 - T_1)/T_3$ if the rest of the energy, $Q_3 \cdot T_1/T_3$, can be disposed of as heat to a heat sink at T_1. The efficiency of this "heat engine" could be defined as $-W/Q_3 = (T_3 - T_1)/T_3$.

Exercise 1.3.3

One mole of a fluid is heated from T_1 to T_2 under constant volume. Show how one can calculate the work done by the surroundings and the heat absorbed from the surroundings. What state function of the fluid do we need to know?

Hint

Since nothing is said about the exchange of work, suppose there is only hydrostatic work.

Solution

The work $-PdV$ is zero if V is constant. The heat is $dQ = dU + PdV = dU$ and we get $Q = \int dU = U_2 - U_1 = U(T_2,V_1) - U(T_1,V_1)$. We must know U as a function of T at constant V.

1.6 *The second law of thermodynamics*

Exercise 1.6.1

In exercise 1.6 suppose the heat of reaction, i.e. the absorption of heat necessary to keep the temperature constant, is ξK. Construct an expression for the total increase of entropy inside the system. Calculate the difference between the total increase of entropy of the system and the internal production of entropy, when ξ increases from zero to the equilibrium value at the experimental temperature.

Hint

Don't calculate each one. The difference can be calculated directly.

Solution

Under constant T and V the heat of reaction must be compensated by heat flow from the surroundings, $Q = \xi K$ and the total increase of entropy is $\Delta S = Q/T + \Delta_{ip}S = \xi K/T + \Delta_{ip}S = -R[\xi\ln\xi - (1 + \xi)\ln(1 + \xi)]$. However, we get the difference directly: $\Delta S - \Delta_{ip}S = Q/T = \xi K/T$. Inserting the equilibrium value of ξ given by the preceding exercise gives $\Delta S - \Delta_{ip}S = (K/T)/[\exp(K/RT) - 1]$.

Exercise 1.6.2

The fact that S is a state function is reflected by the fact that dS can be integrated for a reversible process and the resulting ΔS only depends upon the initial and final states. Show this for an ideal classical gas.

Hint

First, calculate $\mathrm{d}Q$ from the first law. Then use $\mathrm{d}S = \mathrm{d}Q/T$. For one mole of a classical ideal gas $PV = RT$ and $U = A + BT$.

Solution

$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W = \mathrm{d}Q - P\mathrm{d}V$; $\mathrm{d}Q = \mathrm{d}U + P\mathrm{d}V = B\mathrm{d}T + (RT/V)\mathrm{d}V$; $\mathrm{d}S = \mathrm{d}Q/T = (B/T)\mathrm{d}T + (R/V)\mathrm{d}V$. It is interesting to note that by dividing $\mathrm{d}Q$ with T we have thus been able to separate the variables T and V and obtain a state function from Q which is not a state function itself. Integration yields $\Delta S = B\ln(T_2/T_1) + R\ln(V_2/V_1)$.

Exercise 1.6.3

Consider a Carnot cycle with a non-ideal gas and suppose that the process is somewhat irreversible. Use the second law to derive an expression for the efficiency.

Hint

For each complete cycle we have $\Sigma\Delta U = 0$ and $\Sigma\Delta S = 0$ because U and S are both state functions.

Solution

$\Sigma\Delta U = W + Q_1 + Q_3 = 0$; $\Sigma\Delta S = Q_1/T_a + Q_3/T_b + \Delta_{ip}S = 0$ where W is the sum of W_i over the four steps and $\Delta_{ip}S$ is the sum of the internal entropy production over the four steps. We seek $\eta = -W/Q_3$. We can eliminate Q_1, which is negative, by combining the two equations:

$-Q_1 = Q_3T_a/T_b + \Delta_{ip}S\cdot T_a$;
$-W = Q_1 + Q_3 = -Q_3T_a/T_b - \Delta_{ip}S\cdot T_a + Q_3 = Q_3(T_b - T_a)/T_b - \Delta_{ip}S\cdot T_a$

and thus $\eta = -W/Q_3 = (T_b - T_a)/T_b - \Delta_{ip}S\cdot T_a/Q_3 < (T_b - T_a)T_b$ because $\Delta_{ip}S$, T_a and Q_3 are all positive. The efficiency is thus decreased by $\Delta_{ip}S\cdot T_a/Q_3$.

Exercise 1.6.4

Examine if it would be possible to have a system with a spontaneous process such that $\mathrm{d}S$ and $\mathrm{d}Q$ have different signs under spontaneous isothermal conditions. Try to find such a system.

Hint

Start from the second law.

Solution

$T\mathrm{d}S = \mathrm{d}Q + T\mathrm{d}_{\mathrm{ip}}S$. Since $\mathrm{d}_{\mathrm{ip}}S > 0$ we get $T\mathrm{d}S > \mathrm{d}Q$. If $\mathrm{d}Q$ is positive, $\mathrm{d}S$ must also be positive. However, if $\mathrm{d}Q$ is negative, $\mathrm{d}S$ could be positive or negative. In this case it is easier to make $\mathrm{d}S$ positive if the process is only slightly exothermic and if it has a high internal production of entropy. A possible case would be the mixing of two elements to form a solution with a slight negative heat of reaction.

Exercise 1.6.5

We have seen that a perpetuum mobile could be constructed from two reversible heat engines of different efficiencies (if they could be found) by running the less efficient one in reverse. However, this seems impossible and that is why we concluded that all reversible heat engines must have the same efficiency. On the other hand, an irreversible heat engine (i) will have a lower efficiency. It would thus seem tempting to run such an engine in reverse and couple it to a reversible engine (r). Evaluate the net work produced by such an arrangement.

Hint

The net work produced is $-W = -W^r - W^i = Q_1^r + Q_3^r + Q_1^i + Q_3^i = Q_1^r + Q_1^i$ because we should make the size of the irreversible engine such that the heat it delivers to the warm reservoir, $-Q_1^i$, is equal to the heat the reversible engine takes from the same reservoir, Q_3^r, i.e. $Q_3^r + Q_3^i = 0$. Furthermore, for each engine $\Delta S = 0$ for each whole cycle.

Solution

$\Delta S = 0 = Q_3^r / T_b + Q_1^r / T_a$; $\Delta S = 0 = Q_3^i / T_b + Q_1^i / T_a + \Delta S_{ip}$ where $\Delta_{\mathrm{ip}}S$ is the sum of internal entropy production in all four steps. By adding the two equations we get: $(Q_3^r + Q_3^i)/T_b + (Q_1^r + Q_1^i)/T_a + \Delta_{ip}S = 0$. However, $Q_3^r + Q_3^i = 0$ and $-W = -W^r - W^i = Q_1^r + Q_1^i = -\Delta_{ip}S \cdot T_a < 0$ because $\Delta_{\mathrm{ip}}S$ must be positive (second law). One cannot produce work by this arrangement.

1.9 *The combined first and second law*

Exercise 1.9.1

Formulate the combined law for a system, which interacts with the surroundings by means of two pistons working at different pressures.

Hint

One may speculate on what happens inside such a system, i.e. on the nature of the internal process, the progress of which we usually represent by ξ. However, that is not a problem we need to concern ourselves with now.

Solution

The first law becomes $dU = dQ + dW_1 + dW_2 = dQ - P_1dV_1 - P_2dV_2$ and the combined law becomes $dU = TdS - P_1dV_1 - P_2dV_2 - Dd\xi$.

1.11 *Characteristic state functions*

Exercise 1.11.1

Suppose a system, when it transforms between two states without change of the content of matter, can perform some work in addition to $\int PdV$. Show that the maximum amount of work is obtained as the change in Gibbs energy if the two states are at the same pressure and temperature.

Hint

Start with the first law and introduce two kinds of work. If the additional work done on the system is dW_a, then the additional work performed by the system is $- dW_a$. Combine with the second law. In order to keep T and P constant they must be introduced as independent variables.

Solution

$dU = dQ + dW = dQ - PdV + dW_a = TdS - PdV + dW_a - Dd\xi$ where ξ measures the progress of the transformation. Introducing T and P as independent variables yields: $dU - d(TS) + d(PV) = dG = - SdT + VdP + dW_a - Dd\xi$. At constant T,P: $- dW_a = - dG - Dd\xi$. The work performed, $- dW_a$, would be larger the smaller $Dd\xi$ is. The system would thus perform the maximum work if one could arrange that $Dd\xi = 0$ because $Dd\xi$ cannot be negative for a spontaneous process. Then we would get: $- dW_a = - dG$; $- \Delta W_a = G_1 - G_2$.

Exercise 1.11.2

A closed system is contained inside an elastic wall such that $V = V_o(1 - \alpha P)$. Derive the equilibrium condition for an internal process in such a container if the temperature is kept constant.

Hint

Since V_o is a constant and we are going to keep T constant, we should formulate the combined law with T and V_o as the variables and then keep them constant. (Since T is to be constant we do not need to consider the fact that the properties of the wall may depend on T.) First, we introduce V_o instead of P in the expression for dU. Then we must find a function $f(V,V_o)$ such that the dV term in dU vanishes when we subtract df. This function is found by integrating the dV term under constant V_o.

Solution

$P = 1/\alpha - V/\alpha V_o$; $dU = TdS - (1/\alpha - V/\alpha V_o)dV - Dd\xi$. We now want to subtract df from dU where f is a function such that dV will not appear in $d(U - f)$. It is evident that we can choose $f = - V/\alpha + V^2/2\alpha V_o$ and obtain $df = - (1/\alpha - V/\alpha V_o)dV + (V^2/2\alpha)d(1/V_o)$. We also subtract $d(TS)$ and obtain $d(U - TS - f) = TdS - TdS - SdT - (1/\alpha - V/\alpha V_o)dV + (1/\alpha - V/\alpha V_o)dV - (V^2/2\alpha)d(1/V_o) - Dd\xi = - SdT - (V^2/2\alpha)d(1/V_o) - Dd\xi$. Equilibrium at constant T,V_o is given by $D = - (\partial[U - TS - f]/\partial\xi)_{T,V_o}$. The equilibrium condition is thus the minimum of a new function $U - TS + V/\alpha - V^2/2\alpha V_o$.

1.12 *Entropy*

Exercise 1.12.1

Consider two pieces of Zn, one at each end of a sealed silica tube, filled with argon at 1 bar pressure. The ends are kept at different temperatures. One piece may shrink by evaporization and the other grow by condensation. Which one would grow if the principle governing the process were the minimization of *G*? Discuss the conclusion.

Hint

Suppose the vapour pressure of Zn is small enough to be neglected in comparison with 1 bar and thus $dG/dT = - S$.

Solution

With the usual convention, *S* is always positive and thus *G* is lower at the high-*T* end. If Zn would go from higher *G* to lower *G*, it seems that it would evaporate from the cold end and condense at the hot end. However, by experience we know that condensation will occur at the cold end. Actually, there is no basis for the suggestion that *G* should be minimized by a non-isothermal reaction because the difference in *G* depends upon the arbitrary choice of reference for *S*. ΔG between two systems at different temperatures has no physical significance. Instead, the reaction is governed by kinetic factors and depends upon the properties of the substance separating the two pieces, in our case the gas. The vapour pressure of Zn is greater at the higher temperature and Zn will diffuse through the gas from the higher temperature to the lower one.