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Physics 151 Problem Set 4

Problem 18

Problem 2.26. Maximum useful work and free energy changes (Gould and Tobochnik)

(a) Show that if the change in volume of the system is zero, $\Delta V = 0$, and the initial and final temperatures are that of the heat bath, then the maximum useful work is $-\Delta F$.

Solution:

The useful work done W_{useful} is given by

$$W_{\text{useful}} \leq -(\Delta E + P_{\text{bath}}\,\Delta V - T_{\text{bath}}\,\Delta S) \tag{1}$$

such that the maximum useful work is

$$\max W_{\text{useful}} = -\Delta A \tag{2}$$

If there is no change in volume (i.e. $\Delta V = 0$), then the availability becomes

$$\Delta A = \Delta E - T_{\text{bath}}\,\Delta S = \Delta F \tag{3}$$

Therefore, max W_{useful} becomes

$$\max W_{\text{useful}} = -\Delta F \tag{4}$$

(b) Show that if the initial and final temperature and pressure are that of the bath, then the maximum useful work is $-\Delta G$.

Solution:

From the textbook, the Gibbs free energy G is defined as

$$G \equiv E - TS + PV \tag{5}$$

so the change in G is given by

$$\Delta G = \Delta E - \Delta(TS) + \Delta(PV) \tag{6}$$

Since the initial and final temperature and pressure are that of the bath, then the equation above becomes

$$\Delta G = \Delta E - T_{bath}\Delta S + P_{bath}\Delta V \tag{7}$$

and the availability A becomes the Gibbs free energy G:

$$\Delta A = \Delta G \tag{8}$$

Therefore, the maximum useful work done for this case is

$$\max W_{\text{useful}} = -\Delta G \tag{9}$$