

**PS 18: Problem 2.26**

(a) The useful work is defined as

$$W_{\text{useful}} = -(\Delta E + P\Delta V - T_{\text{bath}}\Delta S) \quad (1)$$

If  $\Delta V = 0$ ,

$$W_{\text{useful}} = -(\Delta E - T_{\text{bath}}\Delta S) \quad (2)$$

Recall the Helmholtz free energy:

$$F = E - TS \quad (3)$$

The availability is defined as

$$\Delta A = \Delta F = \Delta E - T_{\text{bath}}\Delta S \quad (4)$$

Substituting (4) into (2),

$$\boxed{W_{\text{useful}} = -\Delta F} \quad (5)$$

(b) Recall the Gibbs free energy:

$$G = E - PV + TS \quad (6)$$

Taking the delta differentials,

$$\Delta G = \Delta E - (P\Delta V + V\Delta P) + (T\Delta S + S\Delta T) \quad (7)$$

If  $\Delta P = \Delta T = 0$ ,

$$\Delta G = \Delta E - P\Delta V + T\Delta S \quad (8)$$

Substituting (8) into (1),

$$\boxed{W_{\text{useful}} = -\Delta G} \quad (9)$$