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THERMODYNAMICS LANDSCAPE SELF STUDY MODULE

Objective

The objective of this module is to set the most general thermodynamics landscape.

Reading assignment

Read Chapter 4 Sandler's Thermodynamics, 4th edition.

Derive

We will derive the energy introduced into a fluid confined in a piston and cylinder assembly by an impeller performing reversible shaft work, subject to different constraints. We will start from the most general form of the Energy balance and the entropy balance to find the answers under different constraints.

$$\frac{dU}{dt} = \sum_{all\ streams} \dot{m}_i\, \hat{H}_i + \dot{Q} + \dot{W}_s - P\frac{dV}{dt}$$

$$\frac{dS}{dt} = \sum_{all\ streams} \dot{m}_i\, \hat{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{generated}$$

Case 1: The system is closed, the process is adiabatic and the system is at constant volume

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{W}_s$$

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The entropy balance indicates that

$$\frac{dS}{dt} = 0$$

This result indicates that for a reversible and adiabatic process, entropy is constant.

Case 2: The system is closed, the process is adiabatic and the system is at constant pressure

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{W}_s - P\frac{dV}{dt}$$

At constant pressure, it is possible to rearrange the expression as

$$\frac{dH}{dt} = \dot{W}_s$$

Similar to case 1,

$$\frac{dS}{dt} = 0$$

Case 3: The system is closed, the process is isothermal and the system is at constant volume

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s$$

While the entropy balance yields

$\frac{dS}{dt} = \frac{\dot{Q}}{T}$ or $\dot{Q} = T\frac{dS}{dt}$ when this expression for $\dot{Q}$ is substituted in the energy balance,

keeping in mind that the temperature is constant, the rearrangement gives

$$\frac{dA}{dt} = \dot{W}_s$$

Where A is the Helmholtz free energy defined by, A=U-TS

It is important to note here that we derive this expression for any fluid. The fact that at

constant temperature U is also constant is valid only for the ideal gases, not for the real fluids.

Therefore we keep U in our derivations.

Case 4: The system is closed, the process is isothermal and the system is at constant pressure

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s - P\frac{dV}{dt}$$

While the entropy balance yields

$\frac{dS}{dt} = \frac{\dot{Q}}{T}$ or $\dot{Q} = T\frac{dS}{dt}$ when this expression for $\dot{Q}$ is substituted in the energy balance,

keeping in mind that the temperature and pressure are constant, the rearrangement gives

$$\frac{dG}{dt} = \dot{W}_s$$

Where A is the Helmholtz free energy defined by, G=U+PV-TS

It is important to note here that we derive this expression for any fluid. The fact that at

constant temperature U is also constant is valid only for the ideal gases, not for the real fluids.

Therefore, we keep U in our expressions.

Now lets combine all of the cases along with their constraints in the table below. Realize that your

independent variables are S, T, P and V and your dependent variables are U, H, A and G. Remember that

for ideal gases the entropy change as a function of T and V are given as follows:

$$\Delta S = n\, C_v \ln\left(\frac{T_2}{T_1}\right) + n\, R \ln\left(\frac{V_2}{V_1}\right)$$

For an ideal gas, V=nRT/P can be substituted into the equation above to get the pressure

equivalent of the expression.

$$\Delta S = n\, C_P \ln\left(\frac{T_2}{T_1}\right) - n\, R \ln\left(\frac{P_2}{P_1}\right)$$

S and V constant	S and P constant
$$\frac{dU}{dt} = \dot{W}_s$$	$$\frac{dH}{dt} = \dot{W}_s$$ H=U+PV
T and V constant	T and P constant
$$\frac{dA}{dt} = \dot{W}_s$$ A=U-TS	$$\frac{dG}{dt} = \dot{W}_s$$ G=U+PV-TS

Calculate

1. Determine the reversible shaft work needed to increase the temperature of a monoatomic

   ideal gas from 300 K to 500 K.

   a. If the process is conducted under constant volume and adiabatic conditions. What is the

      final pressure?

   b. If the process is conducted under constant pressure and adiabatic conditions. What is

      the final volume?

2. A monoatomic ideal gas, initially at 1 atm and 300 K is kept in a 1 L container. Determine the reversible shaft work needed to increase the pressure to 2 atm while keeping the temperature and volume constant.

3. A monoatomic ideal gas, initially at 1 atm and 300 K is kept in a 1 L container. Determine the reversible shaft work needed to increase the volume to 2 liters, while keeping the temperature and pressure constant.

Evaluate yourself

Check if you have answers to the following questions:

1. Why do we need these four different forms of energy, i.e., U, H, G and A?

2. What is the difference between internal energy and enthalpy?

3. What is the difference between Helmholtz free energy and Gibbs Free Energy?

4. Why Helmholtz Free Energy and Gibbs Free Energy are called free energies? What makes them free? Is there a bound energy?

5. Why is entropy an independent variable in the thermodynamic landscape?