

CH365 Chemical Engineering Thermodynamics

Lesson 23

Calculation of Entropy and Entropy Changes for an Ideal Gas

Summary of Section 5.4

There exists a property called entropy S , which is an intrinsic property of a system, functionally related to the measurable coordinates characterizing the system. For a reversible process, changes in this property are given by Eq. 5.1.

$$dS^t = \frac{dQ_{\text{rev}}}{T} \quad \text{Eq. 5.1} \quad (\text{Axiom to 2}^{\text{nd}} \text{ Law})$$

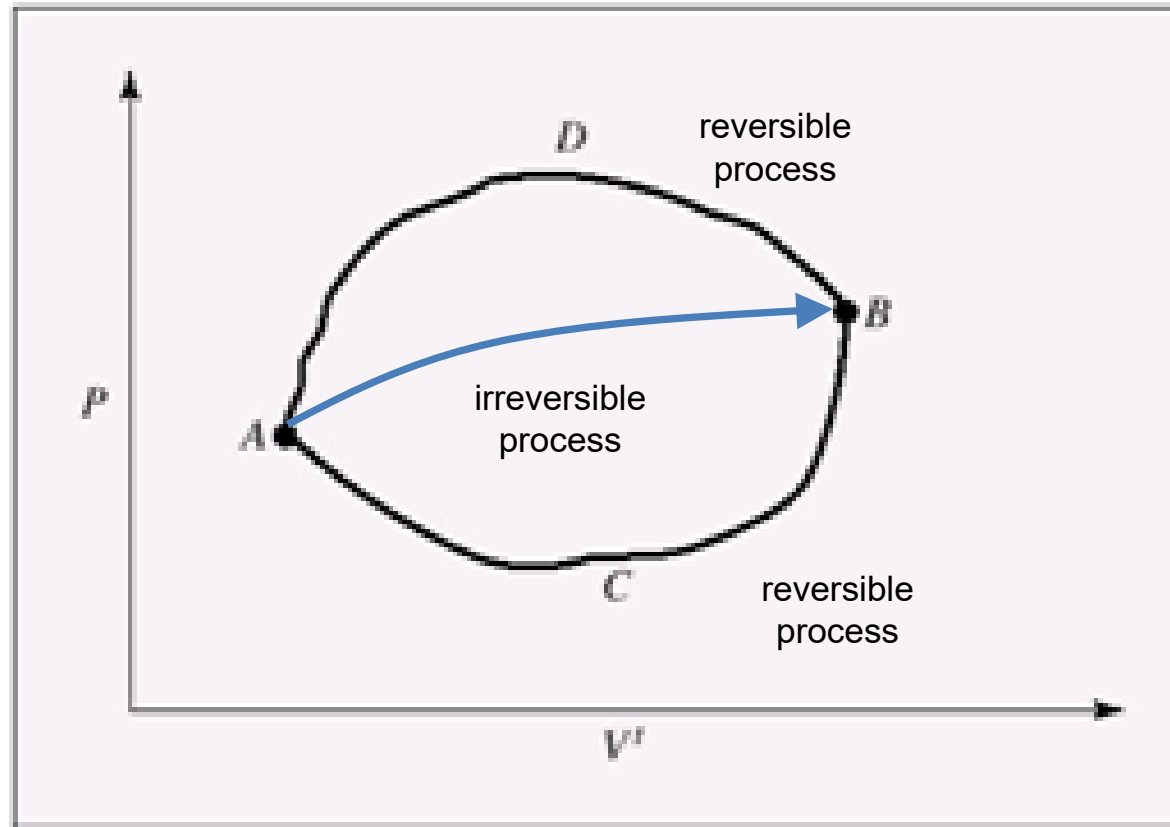
The change in entropy for any system undergoing a finite reversible process is:

$$\Delta S^t = \int \frac{dQ_{\text{rev}}}{T} \quad \text{Integral of Eq. 5.1}$$

When a system undergoes an irreversible process between two equilibrium states, the irreversible path cannot be directly integrated. The entropy change of the system is evaluated by integrating Eq. 5.1 along an arbitrarily chosen reversible process that accomplishes the same change of state as the actual process. Because entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.

Independent of Path – State Function

$$dS^t = \frac{dQ_{\text{rev}}}{T}$$



$$\Delta S^t_{ACB} = \int_{ACB} \frac{dQ_{\text{rev}}}{T}$$

$$\Delta S^t_{ADB} = \int_{ADB} \frac{dQ_{\text{rev}}}{T}$$

$$\Delta S^t_{AB} = \Delta S^t_{ACB} = \Delta S^t_{ADB}$$

true for irreversible processes
as well as reversible

Entropy Changes for an Ideal Gas

$$dU = dQ_{\text{rev}} - PdV \quad \text{First Law, Eq. 2.7, reversible}$$

$$H = U + PV \quad \text{Definition of enthalpy, Eq. 2.10}$$

$$dH = dU + PdV + VdP \quad \text{Differentiate}$$

$$dH = dQ_{\text{rev}} - \cancel{PdV} + \cancel{PdV} + VdP = dQ_{\text{rev}} + VdP$$

$$dQ_{\text{rev}} = dH - VdP \quad dH = C_P^{\text{ig}} dT \quad \text{and} \quad V = \frac{R \cdot T}{P}$$

$$dQ_{\text{rev}} = C_P^{\text{ig}} \cdot dT - R \cdot T \cdot \frac{dP}{P}$$

$$\frac{dQ_{\text{rev}}}{T} = C_P^{\text{ig}} \frac{dT}{T} - R \cdot \frac{dP}{P} \quad dS = \frac{dQ_{\text{rev}}}{T} \quad \text{Eq. 5.1}$$

$$dS = C_P^{\text{ig}} \frac{dT}{T} - R \cdot \frac{dP}{P}$$

$$\frac{dS}{R} = \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} - d \ln P \quad \longleftrightarrow \quad \frac{\Delta S}{R} = \int_{T_0}^T \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} - \ln \frac{P}{P_0} \quad \text{Eq. 5.10}$$

Integrated Forms

$$\text{ICPS} = \int_{T_0}^T \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} = A \cdot \ln \frac{T}{T_0} + \left[B + \left(C + \frac{D}{T_0^2 T^2} \right) \cdot \left(\frac{T + T_0}{2} \right) \right] \cdot (T - T_0) \quad \text{Eq. 5.11}$$

$$\text{MCPS} = \frac{\langle C_P^{\text{ig}} \rangle_s}{R} = A + \left[B + \left(C + \frac{D}{T_0^2 T^2} \right) \cdot \left(\frac{T + T_0}{2} \right) \right] \cdot \left(\frac{T - T_0}{\ln(T / T_0)} \right) \quad \text{Eq. 5.13}$$

$$\text{where } \langle C_P^{\text{ig}} \rangle_s = \frac{\int_{T_0}^T C_P^{\text{ig}} dT / T}{\ln(T / T_0)} \quad \text{Eq. 5.12}$$

$$\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} - \ln \frac{P}{P_0}$$

Eq. 5.10

$$\frac{\Delta S}{R} = \text{ICPS} - \ln \frac{P}{P_0}$$

$$\frac{\Delta S}{R} = \text{MCPS} \cdot \ln \left(\frac{T}{T_0} \right) - \ln \frac{P}{P_0}$$

Eq. 5.14

Example 5.4

Methane gas at 550 K and 5 bar undergoes a reversible adiabatic expansion to 1 bar. Assuming methane to be an ideal gas at these conditions, find its final temperature.

$$\frac{\Delta S}{R} = \text{MCPS} \cdot \ln\left(\frac{T}{T_0}\right) - \ln \frac{P}{P_0} \quad \text{Eq. 5.14}$$

$$\text{MCPS} = \frac{\langle C_P^{\text{ig}} \rangle_S}{R} = A + \left[B + \left(C + \frac{D}{T_0^2 T^2} \right) \cdot \left(\frac{T + T_0}{2} \right) \right] \cdot \left(\frac{T - T_0}{\ln(T / T_0)} \right) \quad \text{Eq. 5.13}$$

T_0 , P_0 , and P are all known

T is the only unknown

Solve in Mathematica

Example 5.4

```
R = 8.314; (*J/mol*K*)
```

```
a = 1.702;
```

```
b = 9.081 * 10-3;
```

```
c = -2.164 * 10-6;
```

```
d = 0 * 105;
```

```
T0 = 550; (*K*)
```

```
P0 = 5; (*bar*)
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```
P = 1; (*bar*)
```

$$\text{MCPS} = a + \left(b + \left(c + \frac{d}{T_0^2 * T^2} \right) * \left(\frac{T + T_0}{2} \right) \right) * \left(\frac{T - T_0}{\text{Log}[T / T_0]} \right);$$

```
In[24]:= eq1 = 0 == MCPS * Log[T / T0] - Log[ $\frac{P}{P_0}$ ];
```

```
In[23]:= Solve[eq1, T, Reals] // Quiet
```

```
Out[23]= { { T → 411.3344399 }, { T → 8567.069029 } }
```

411.3344399
ANS, K

Questions

Homework

Problem 5.8

With respect to 1 kg of liquid water:

(a) Initially at 0 deg C, it is heated to 100 deg C by contact with a heat reservoir at 100 deg C. What is the entropy change of the water? What is the entropy change of the heat reservoir? What is ΔS_{total} ?

(b) Initially at 0 deg C, it is first heated to 50 deg C by contact with a heat reservoir at 50 deg C, and then heated to 100 deg C by contact with a heat reservoir at 100 deg C. What is ΔS_{total} ?

(c) Explain how the water might be heated from 0 deg C to 100 deg C so that $\Delta S_{\text{total}} = 0$.

$$C_{P,\text{water}} = 4.184 \frac{\text{kJ}}{\text{kg} \cdot \text{C}} = 4.184 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

Problem 5.10

An ideal gas, $C_P = (7/2)R$, is heated in a steady-flow heat exchanger from 70 deg C to 190 deg C by another stream of the same gas, which enters at 320 deg C. The flow rates of the two streams are the same, and heat losses from the exchanger are negligible.

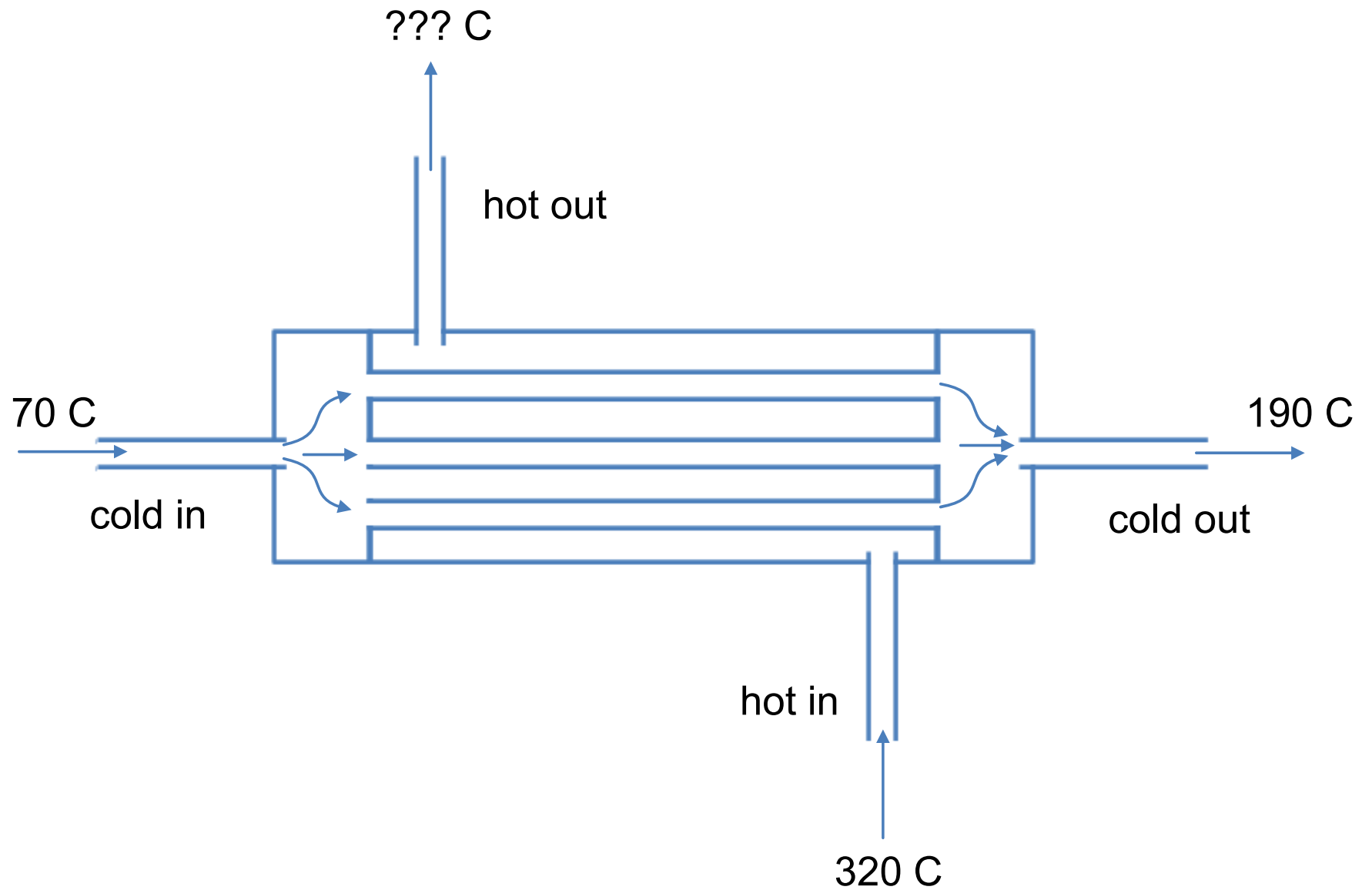
(a) Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger.

(b) What is ΔS_{total} in each case?

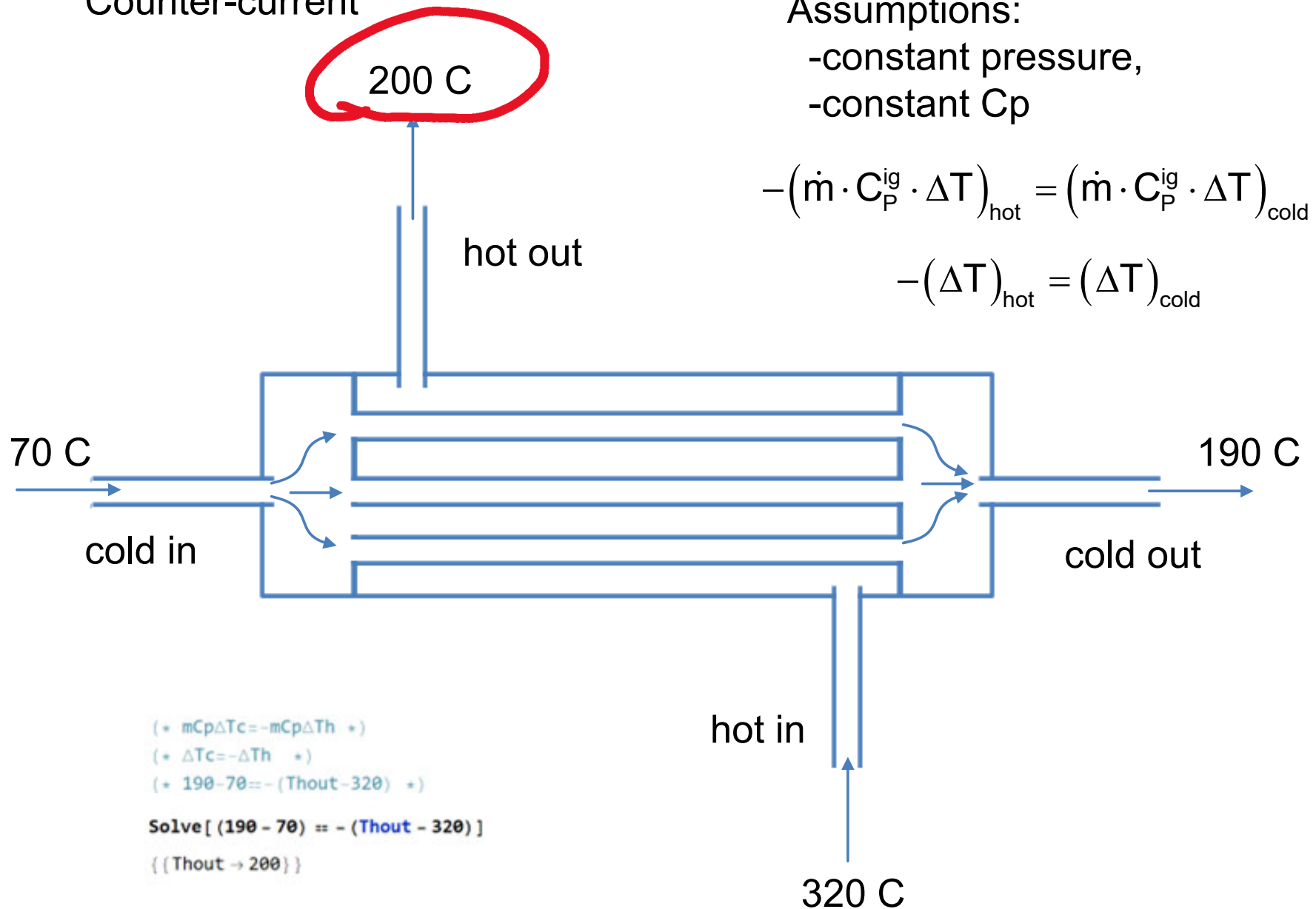
(c) Repeat parts (a) and (b) for countercurrent flow if the heating stream enters at 200 deg C.

Assume pressure drop is negligible. Not a good assumption but needed.

Counter-current

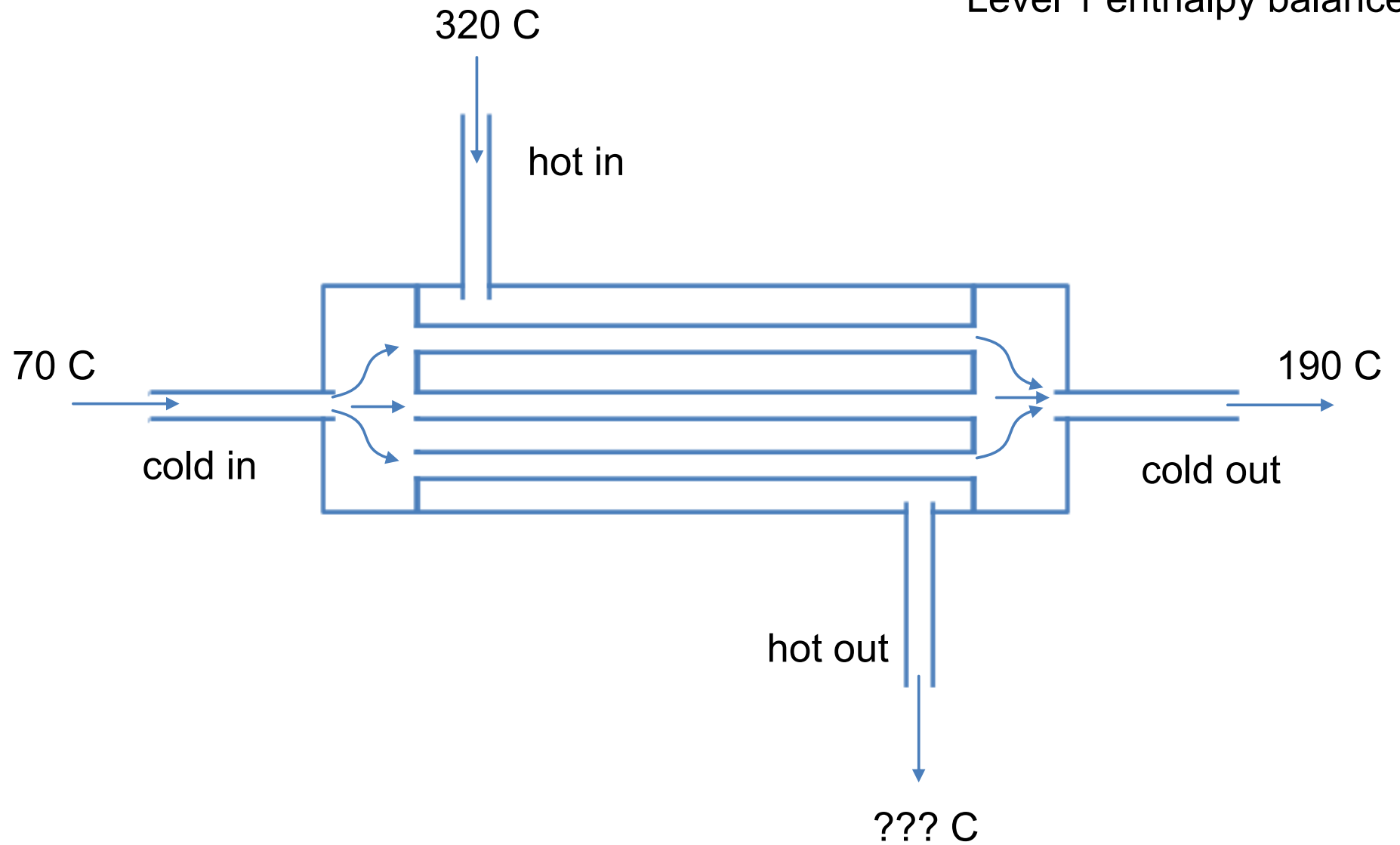


Counter-current



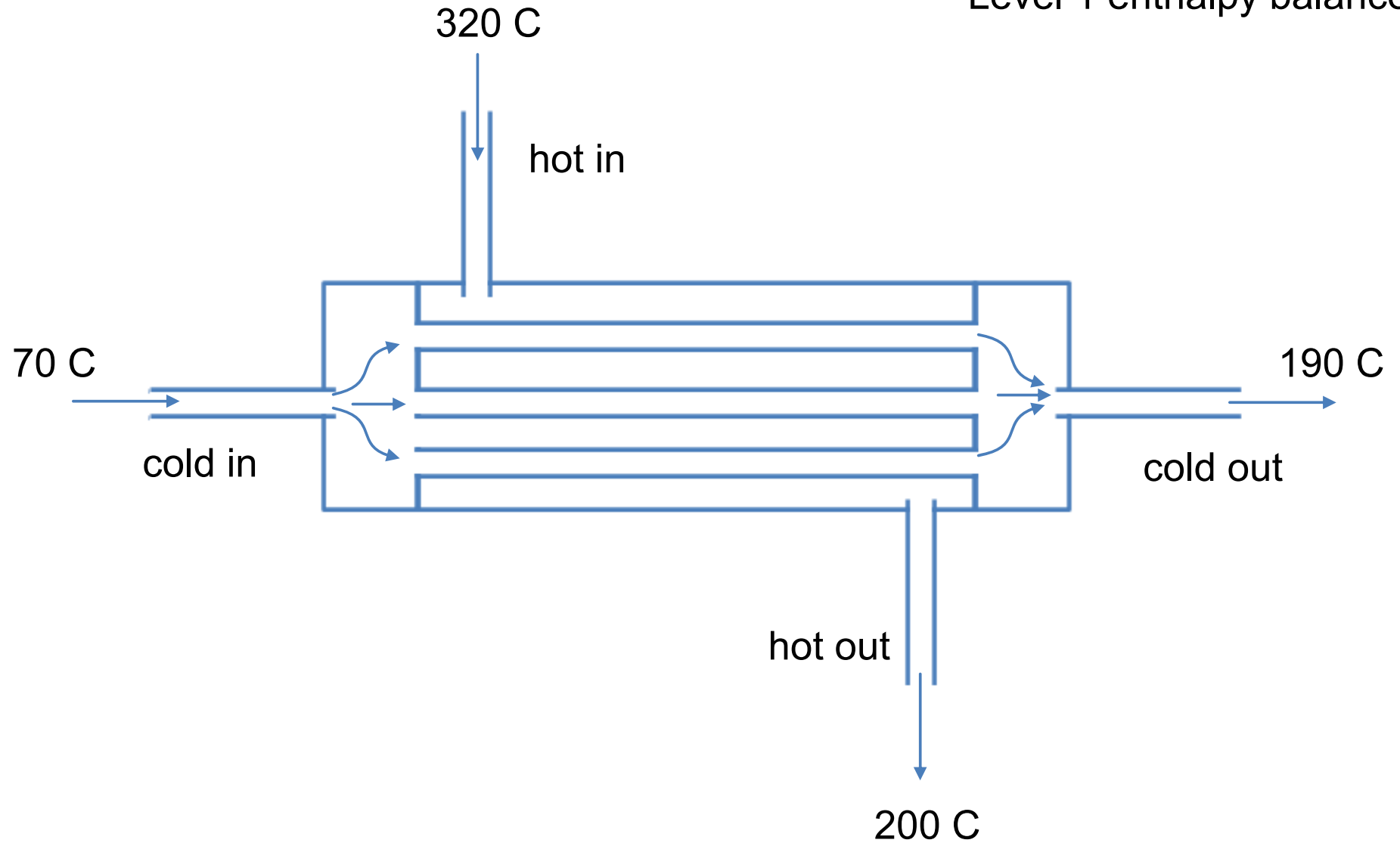
Co-current

Level 1 enthalpy balance



Co-current

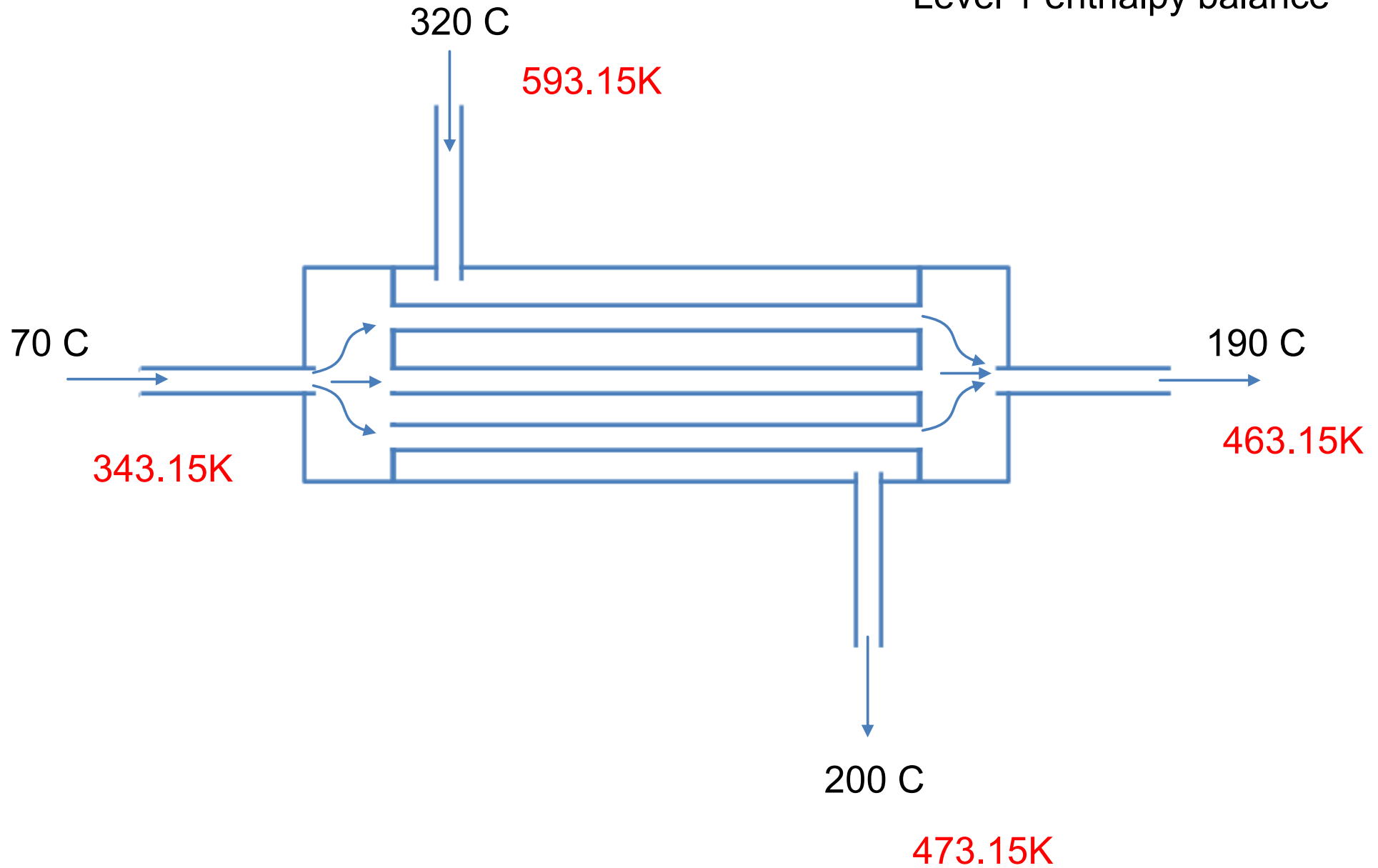
Level 1 enthalpy balance



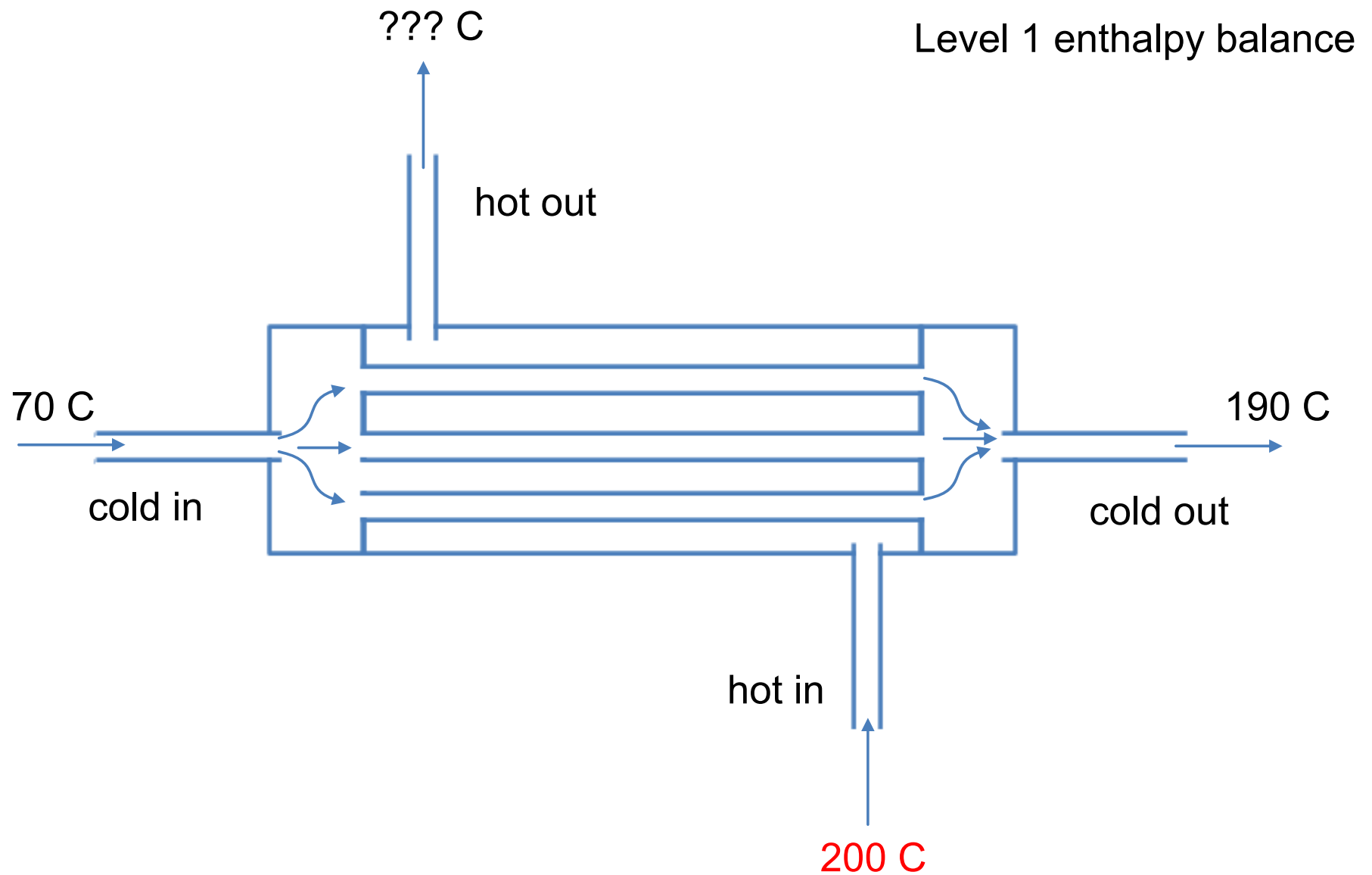
All T's must be in K

Co-current

Level 1 enthalpy balance



Part (c), counter-current



Counter-current

Level 1 enthalpy balance

