

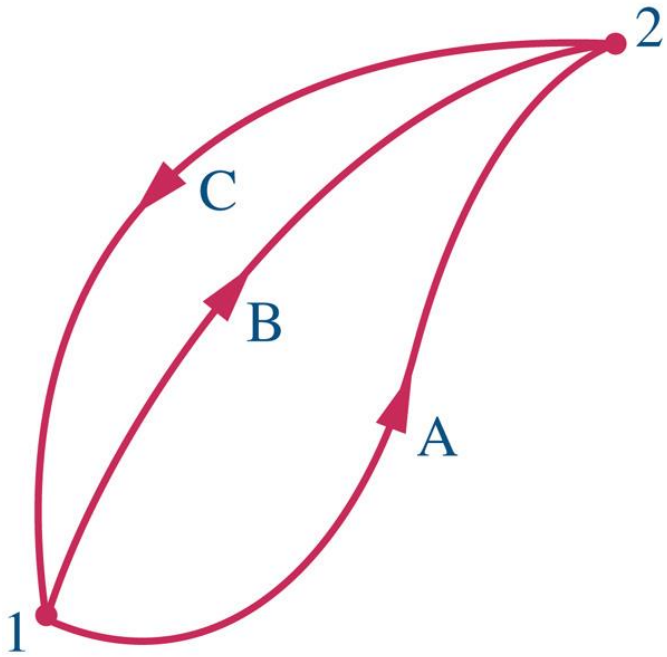
Cap. 6: Utilizando a Entropia

O corolário de Clausius ou Desigualdade de Clausius

$$\oint \left(\frac{\delta Q}{T} \right)_f \leq 0 \qquad \oint \left(\frac{\delta Q}{T} \right)_f + \sigma_{ciclo} = 0$$

- δQ representa o calor trocado através de uma região da fronteira do sistema num instante durante o ciclo;
- T é a temperatura absoluta dessa região da fronteira;
- f enfatiza que as quantidades dentro da integral são computadas na fronteira;
- \oint indica que a integral deve ser tomada sobre todas as partes da fronteira e durante o ciclo inteiro.
- A igualdade se aplica ao caso quando não há irreversibilidades internas, a desigualdade se aplica quando há irreversibilidades no sistema.

Equação de balanço de entropia para sistema fechados



$$\oint \left(\frac{\delta Q}{T} \right)_f \leq 0$$

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T_f} + \sigma_2$$

$$\frac{dS}{dt} = \sum \frac{\dot{Q}_i}{T_{f,i}} + \dot{\sigma}$$

2° Lei: Entropia

- Para um ciclo

$$\oint \left(\frac{\delta Q}{T} \right)_f \leq 0$$

- ou

$$\int \left(\frac{\delta Q}{T} \right)_f + \sigma_{ciclo} = 0$$

- $\sigma_{ciclo} = 0$ sem irreversibilidade
- $\sigma_{ciclo} > 0$ com irreversibilidade
- $\sigma_{ciclo} < 0$ impossível

Entropia

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T} \right)_{\text{int rev}}$$

[J/K]

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{int rev}}$$

Equações de balanço de entropia

Sistemas fechados

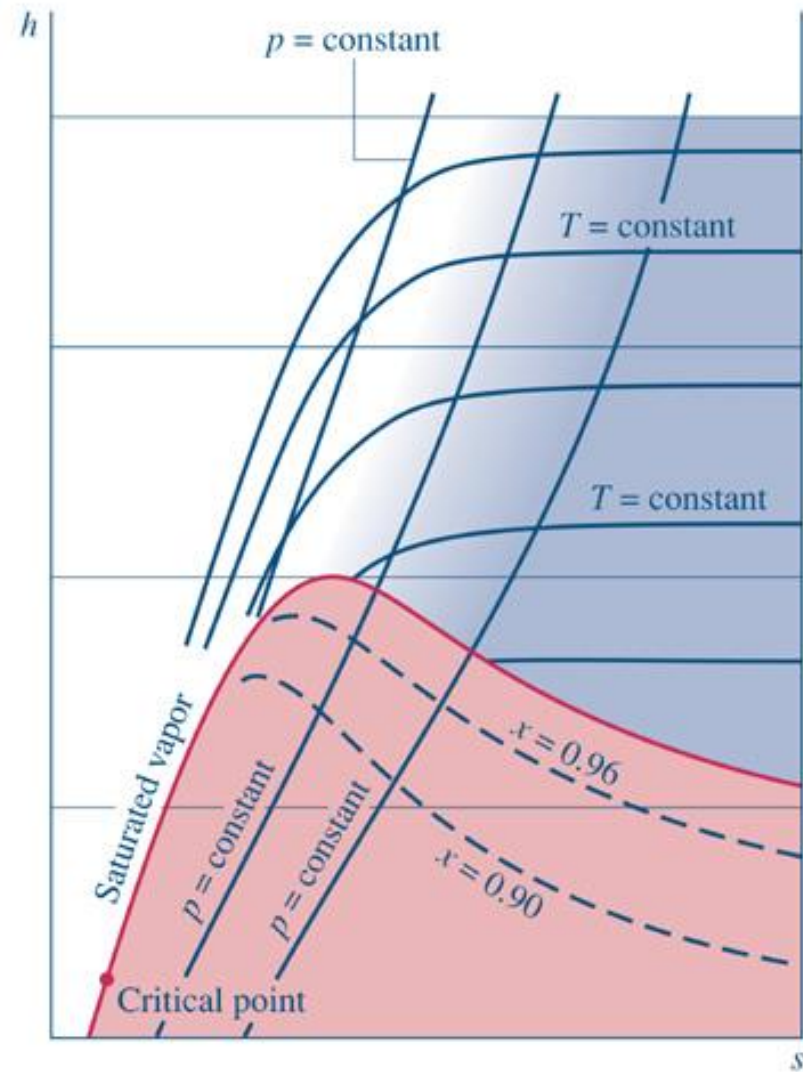
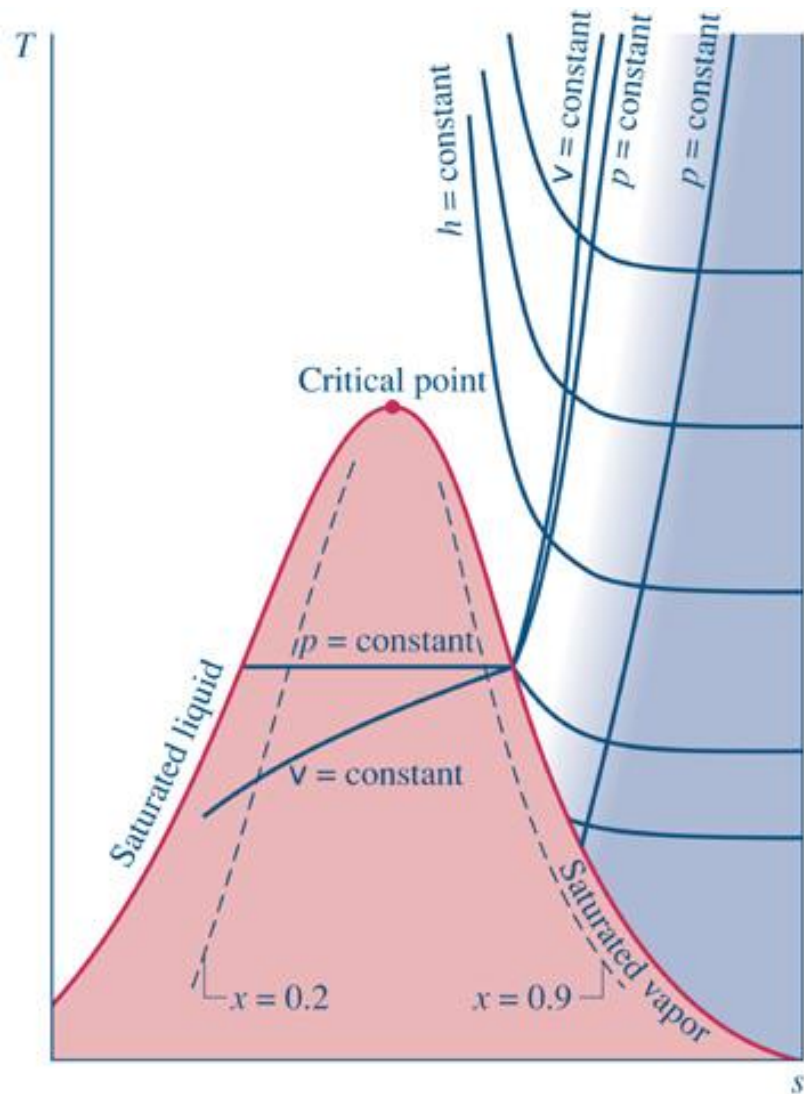
$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T_f} + \sigma_2$$

$$\frac{dS}{dt} = \sum \frac{\dot{Q}_i}{T_{f,i}} + \dot{\sigma}$$

Volumes de controle

$$\frac{dS}{dt} = \sum \frac{\dot{Q}_i}{T_{f,i}} + \sum \dot{m}_e s_e - \sum \dot{m}_s s_s + \dot{\sigma}$$

Diagrama Ts e Diagrama de Mollier (h s)



Relações de Maxwell

- Entropia $\delta Q = T dS$
- Trabalho $\delta W = p dV$
- 1° Lei $\delta Q - \delta W = dU$
- Entalpia $dH = dU + d(pV) = dU + p dV + V dp$

- Na 1° Lei $T dS - p dV = dU$
» ou $T dS = dU + p dV$

- Da entalpia $T dS = dH - V dp$

Relações de Maxwell

- Normalmente

$$u=f(T,v)$$

$$h = u + pv = f(T, p)$$

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp$$

- Para um gás ideal

$$\left(\frac{\partial u}{\partial v} \right)_T = 0$$

Relações de Maxwell

- Então para um gás ideal

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT = c_v dT$$

$$h = u(T) + pv = u(T) + RT$$

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT = c_p dT$$

Varição de Entropia para uma Substância Incompressível

$$\left\{ \begin{array}{l} T ds = du + \cancel{p dv}^0 \\ du = c(T) dT \end{array} \right.$$

$$ds = c(T) \frac{dT}{T}$$

integrando

$$s_2 - s_1 = \int_1^2 c(T) \frac{dT}{T} = c \ln \frac{T_2}{T_1}$$

Sendo
 c constante

Variação de Entropia para um gás perfeito

$$\left\{ \begin{array}{l} T ds = du + p dv \\ du = c_v dT \end{array} \right.$$

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

integrando

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \left(\frac{v_2}{v_1} \right)$$

Varição de Entropia para um gás perfeito

$$\left\{ \begin{array}{l} T ds = dh - v dp \\ dh = c_p dT \end{array} \right.$$

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p}$$

integrando

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \left(\frac{p_2}{p_1} \right)$$

Obtendo valores de entropia a partir de valores de referência

- A partir de $s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \left(\frac{p_2}{p_1} \right)$

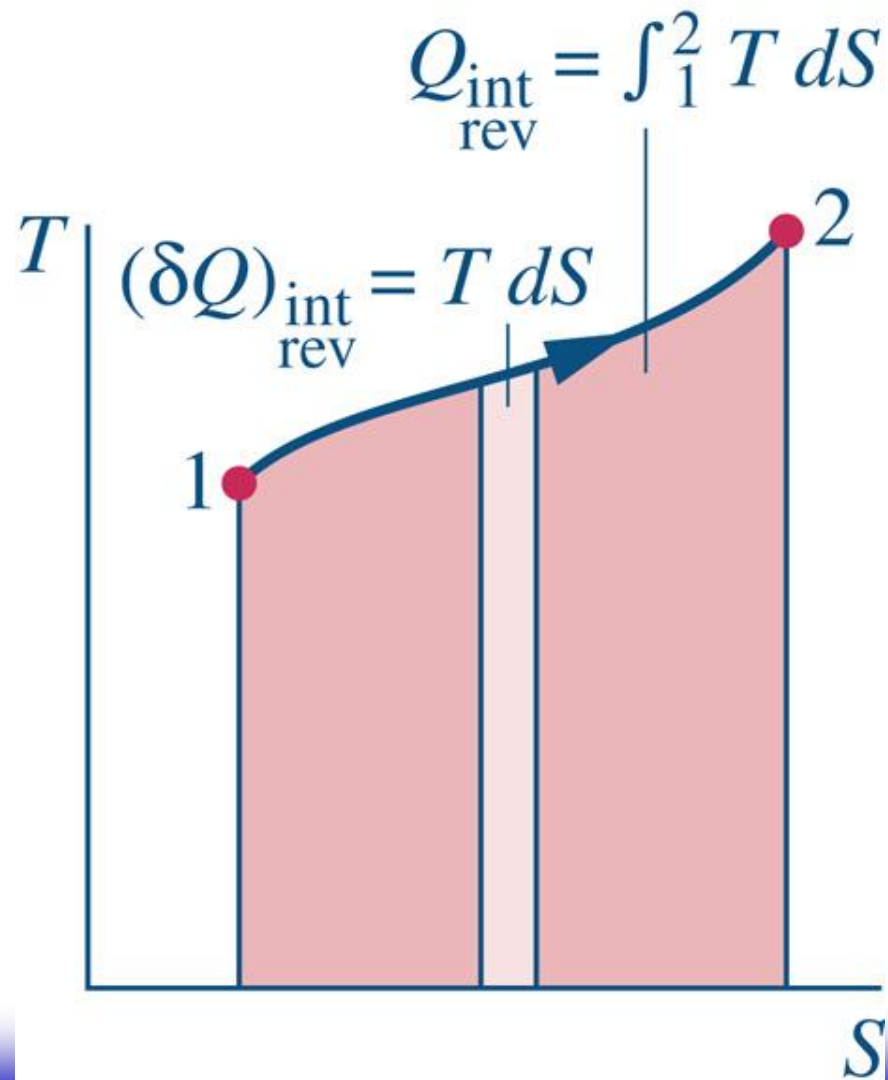
- Utilizando uma temperatura intermediária onde

$$\int_{T_1}^{T_2} c_p \frac{dT}{T} = \int_{T_1}^{T'} c_p \frac{dT}{T} + \int_{T'}^{T_2} c_p \frac{dT}{T} = \int_{T'}^{T_2} c_p \frac{dT}{T} - \int_{T'}^{T_1} c_p \frac{dT}{T}$$

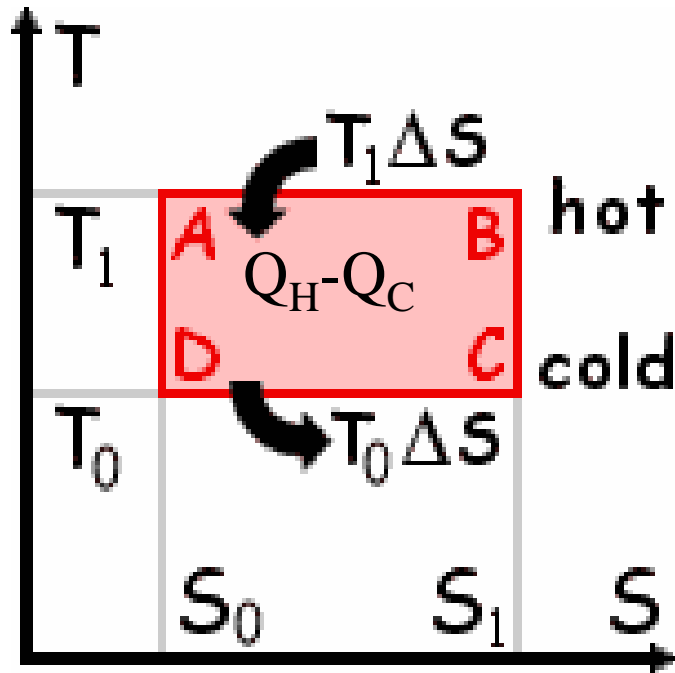
$$s^o(T) = \int_{T'}^T c_p \frac{dT}{T} \quad \int_{T_1}^{T_2} c_p \frac{dT}{T} = s^o(T_2) - s^o(T_1)$$

$$s(T_2, p_2) - s(T_1, p_1) = s^o(T_2) - s^o(T_1) - R \ln \left(\frac{p_2}{p_1} \right)$$

Área do diagrama T_s



Ciclo de Carnot: Diagrama T-s

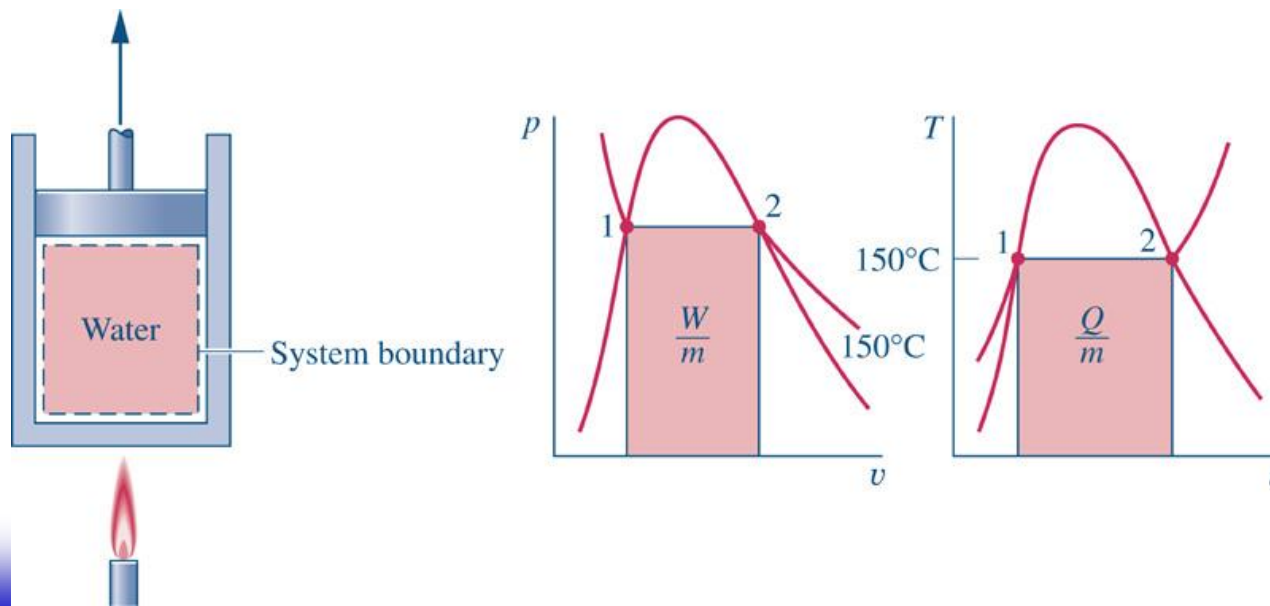


$$\delta Q_{rev} = TdS$$

- **Carnot's Ideal Engine: The Carnot Cycle.**
- **Hot** (A to B) *slow* isothermal expansion. The hot gas performs work and receives a quantity of heat $T_1 \Delta S$.
- **Cooling** (B to C) adiabatic expansion. The gas keeps working without any exchange of heat.
- **Cold** (C to D) *slow* isothermal compression. The cold gas receives work and gives off (wasted) heat $T_0 \Delta S$.
- **Heating** (D to A) adiabatic compression from outside work (flywheel) returns the gas to the initial hot state A.

Exemplo 6.1: Avaliando o trabalho e o calor em um processo internamente reversível para a água

- Água, inicialmente como líquido saturado a 150°C ($423,15\text{K}$) está contida em um conjunto cilindro-pistão. A água é submetida a um processo que leva ao estado correspondente de vapor saturado, durante o qual o pistão se move livremente ao longo do cilindro. Considerando que a mudança de estado acontece em virtude do aquecimento da água à medida que esta percorre um processo internamente reversível a pressão e temperatura constantes, determine o trabalho e a quantidade de calor transferida por unidade de massa.



Balanço de entropia em sistemas fechados

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T} \right)_{\text{fronteira}} + \sigma$$



Varição
de entropia



Transferência de
entropia
pela fronteira

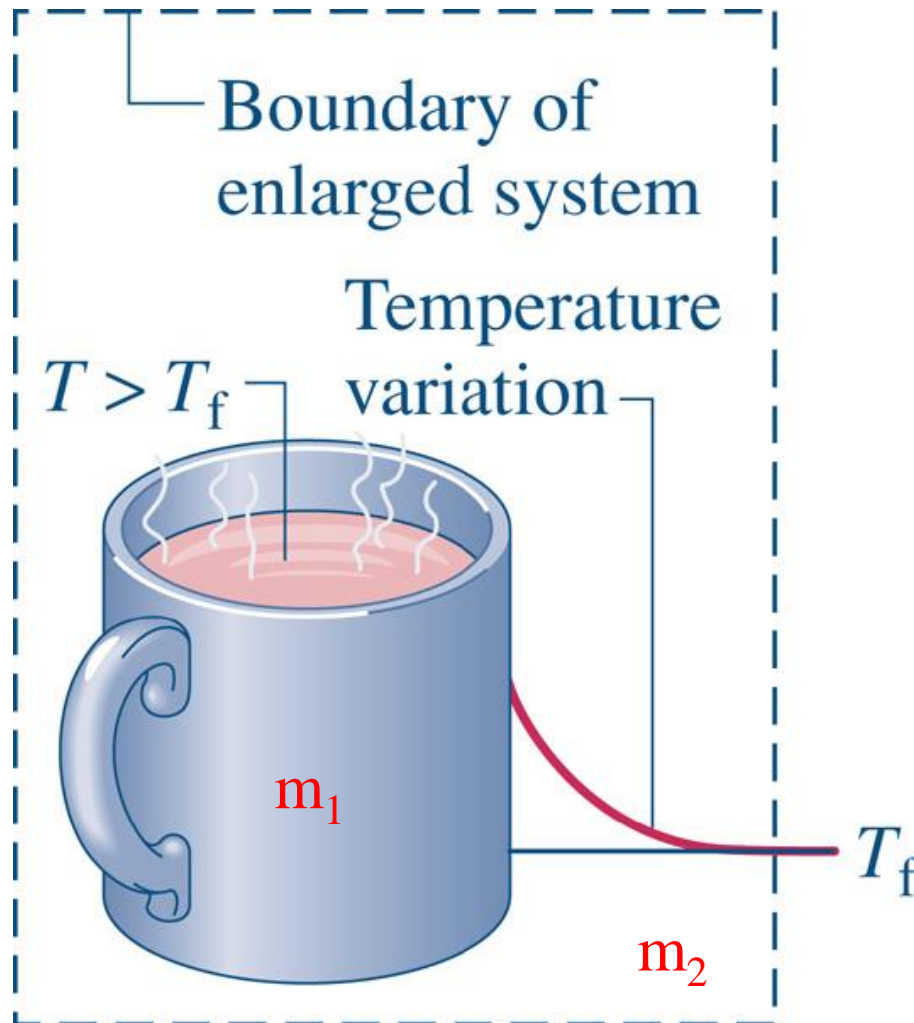


geração de
entropia

- $\sigma=0$ sem irreversibilidade
- $\sigma>0$ com irreversibilidade
- $\sigma<0$ impossível

$$S_2 - S_1 = \begin{cases} > 0 \\ = 0 \\ < 0 \end{cases}$$

Avaliando a geração de entropia em sistemas fechados

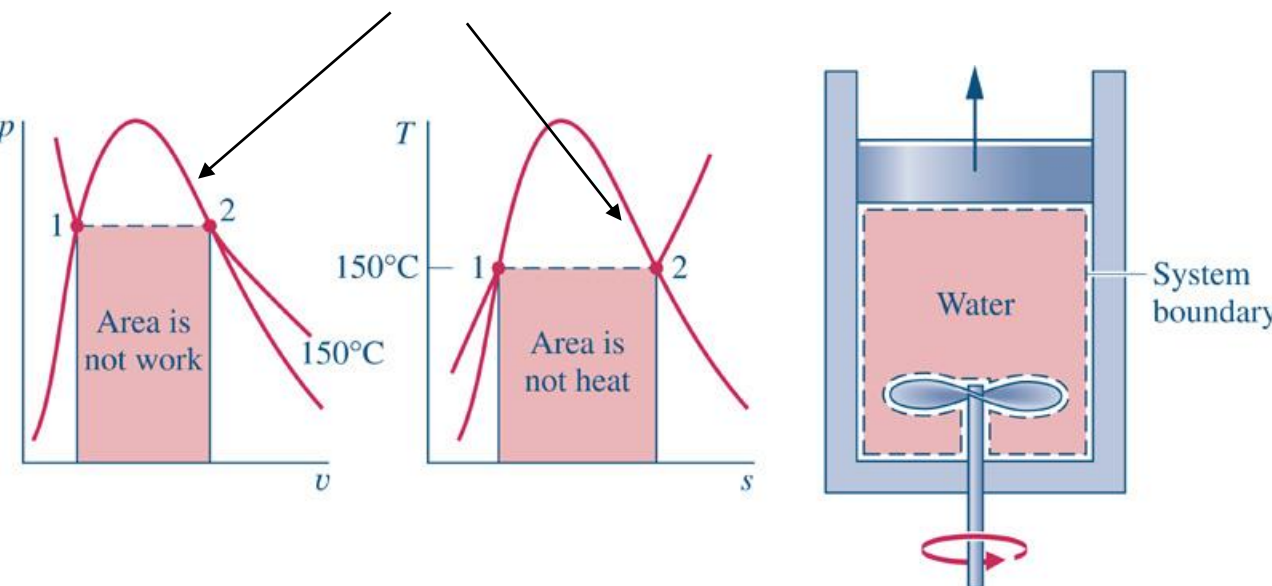


$$\Delta S = \frac{Q}{T_f}$$

Exemplo 6.2: Trabalho e geração de entropia em um processo irreversível

- Água, inicialmente como líquido saturado a 150°C (423,15K) está contida em um conjunto cilindro-pistão. A água é submetida a um processo que leva ao estado correspondente de vapor saturado, durante o qual o pistão se move livremente ao longo do cilindro. Não ocorre transferência de calor para a vizinhança. Se a mudança de fase ocorrer pela ação de um agitador, determine o trabalho líquido por unidade de massa e a quantidade de entropia produzida por unidade de massa.

Não representa o processo



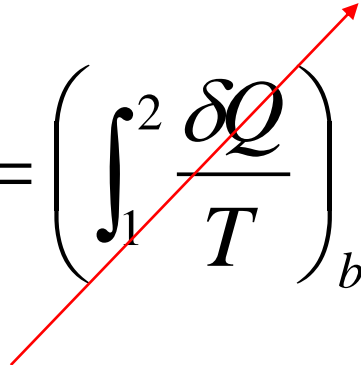
$$\Delta U + \cancel{\Delta EC} + \cancel{\Delta EP} = \cancel{Q} - W$$

$$\frac{W}{m} = -(u_2 - u_1)$$

$$\frac{W}{m} = -(2559,5 - 631,68)$$

$$\frac{W}{m} = -1927,83 \text{ kJ/kg}$$

Exemplo 6.2: Trabalho e geração de entropia em um processo irreversível

$$\Delta S = \left(\int_1^2 \frac{\delta Q}{T} \right)_b + \sigma$$


$$\frac{\sigma}{m} = s_2 - s_1$$

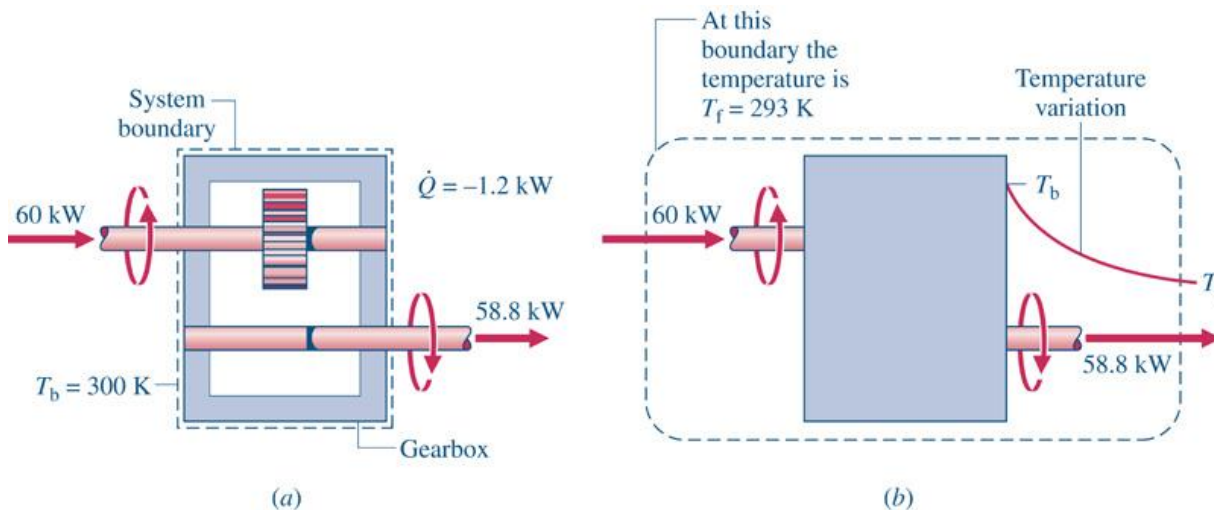
$$\frac{\sigma}{m} = 6,8379 - 1,8418 = 4,9961 \frac{\text{kJ}}{\text{kg K}}$$

Balanço da Taxa de Entropia em Sistemas Fechados

$$\frac{dS}{dt} = \sum_j \frac{\delta \dot{Q}_j}{T_j} + \dot{\sigma}$$

Exemplo 6.4: Identificando Irreversibilidades

- Avalie a taxa de geração de entropia $\dot{\sigma}$, para:
- a) Uma caixa de redução como a figura.
- b) Um sistema estendido que consiste na caixa de redução e em uma parcela suficiente de sua vizinhança, de maneira que a transferência de calor ocorra à temperatura da vizinhança que se encontra afastada da caixa de redução.
- $T_f = 293 \text{ K}$ (20°C)



$$\frac{dS}{dt} = \sum_j \frac{\delta \dot{Q}_j}{T_j} + \dot{\sigma}$$

$$\dot{\sigma} = \frac{\delta \dot{Q}}{T_b}$$

a)
$$\dot{\sigma} = \frac{-(-1,2) \text{ kW}}{300 \text{ K}} = 4 \text{ W / K}$$

b)
$$\dot{\sigma} = \frac{-(-1,2) \text{ kW}}{293 \text{ K}} = 4,1 \text{ W / K}$$

Sentido dos processos: Princípio do Aumento de Entropia

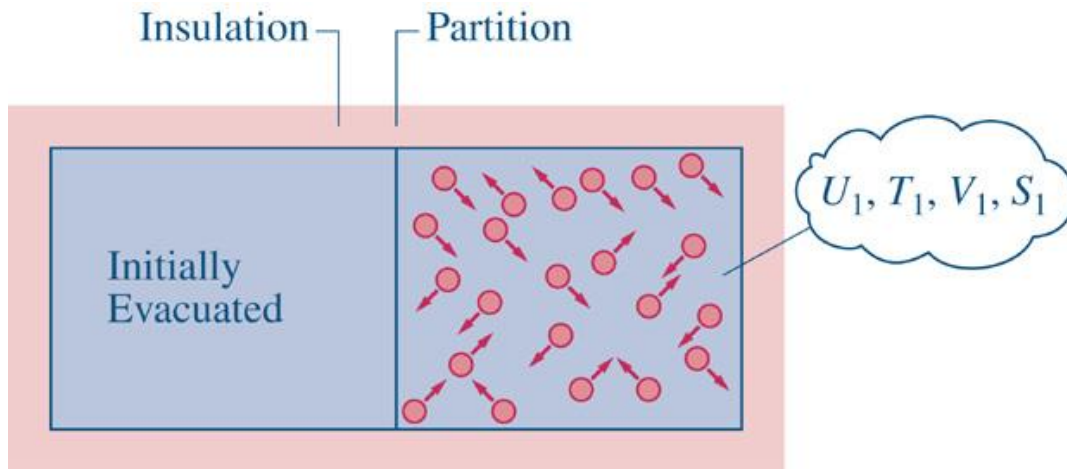
$$\Delta E \Big|_{isolado} = 0; \quad \Delta E \Big|_{sistema} + \Delta E \Big|_{viz} = 0$$

$$\Delta S \Big|_{isolado} = \left(\int_1^2 \frac{\delta Q}{T} \right)_b + \sigma_{isolado}$$

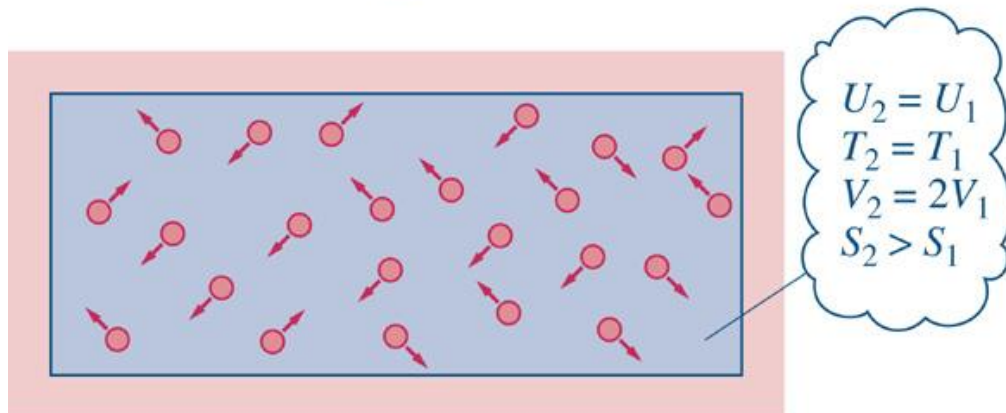
$$\Delta S \Big|_{sistema} + \Delta S \Big|_{viz} = \sigma_{isolado} \quad (+)$$

- O princípio do aumento de entropia estabelece o sentido no qual qualquer processo deve evoluir (naturalmente). Os processos (naturais) ocorrem somente no sentido que faz aumentar o somatório da entropia do sistema com a entropia da vizinhança.
- A entropia de um sistema isolado *umenta* à medida que o estado de equilíbrio é alcançado: Máxima entropia.

Interpretação Microscópica da Entropia



(a)



(b)

- Relação de Boltzmann

$$(S_2 - S_1)/N = k \ln(w_2/w_1)$$

w : número de microestados possíveis

N : número de partículas

k : Constante de Boltzmann

$$= 1,3806488 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

Ludwig Eduard Boltzmann

- Ludwig Eduard Boltzmann (Viena, 20 de fevereiro de 1844 — Duino-Aurisina, 5 de setembro de 1906) foi um físico austríaco, conhecido pelo seu trabalho nos campo da **termodinâmica estatística**. É considerado junto com Josiah Willard Gibbs e James Clerk Maxwell como o fundador da mecânica estatística. Foi defensor da teoria atômica, numa época em que esta ainda era bem controversa.
- Boltzmann sofria de enorme instabilidade emocional, alternando fases de depressão com outras de enorme excitação ou irritação e pensa-se que sofria muito provavelmente de distúrbio bipolar. Lise Meitner afirmou que as pessoas mais próximas dele conheciam os seus ataques de depressão profunda e as suas tentativas de suicídio falecendo em 5 de Setembro de 1906, num ataque de depressão. Ele foi enterrado em Viena e na sua tumba está escrita a famosa equação da física estatística $S = k \log W$.



Balanço da Taxa de Entropia para Volume de Controle

$$\left. \frac{dS}{dt} \right|_{VC} = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_e \dot{m}_e s_e - \sum_s \dot{m}_s s_s + \dot{\sigma}_{VC}$$



Taxa de
variação
de entropia



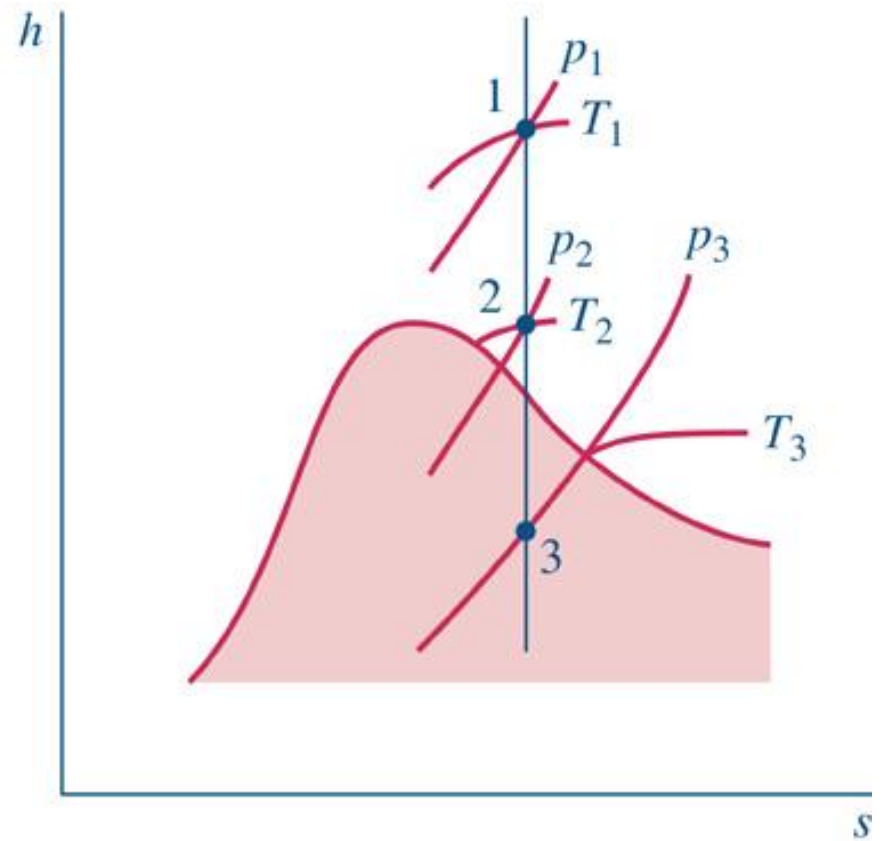
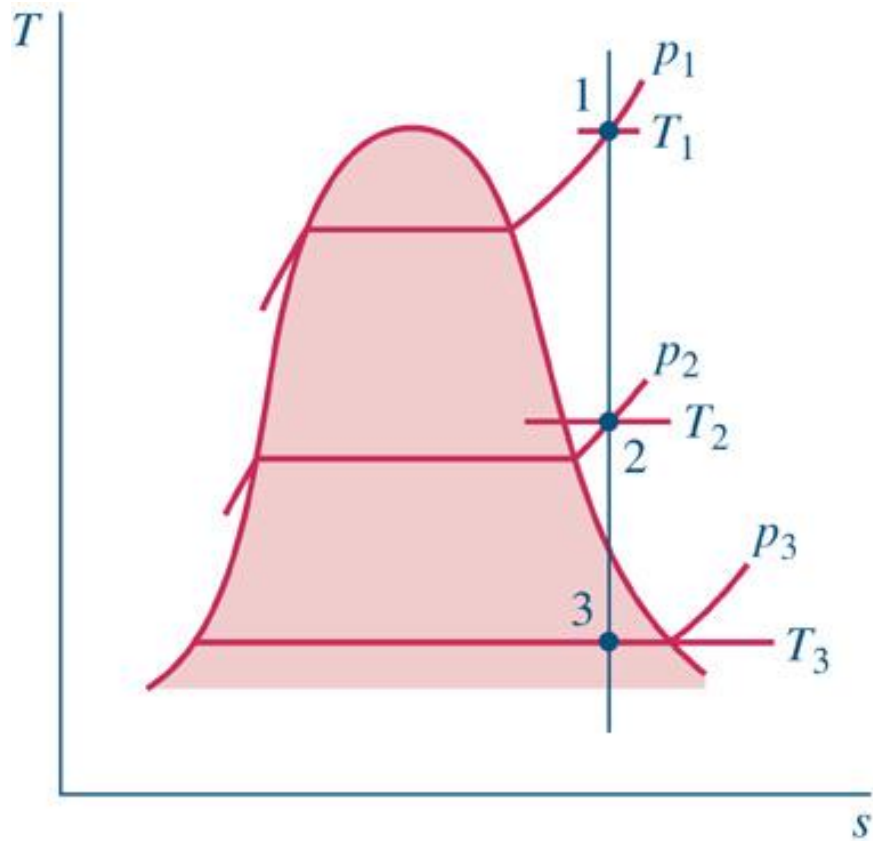
Taxa de
transferência de
entropia
pela fronteira



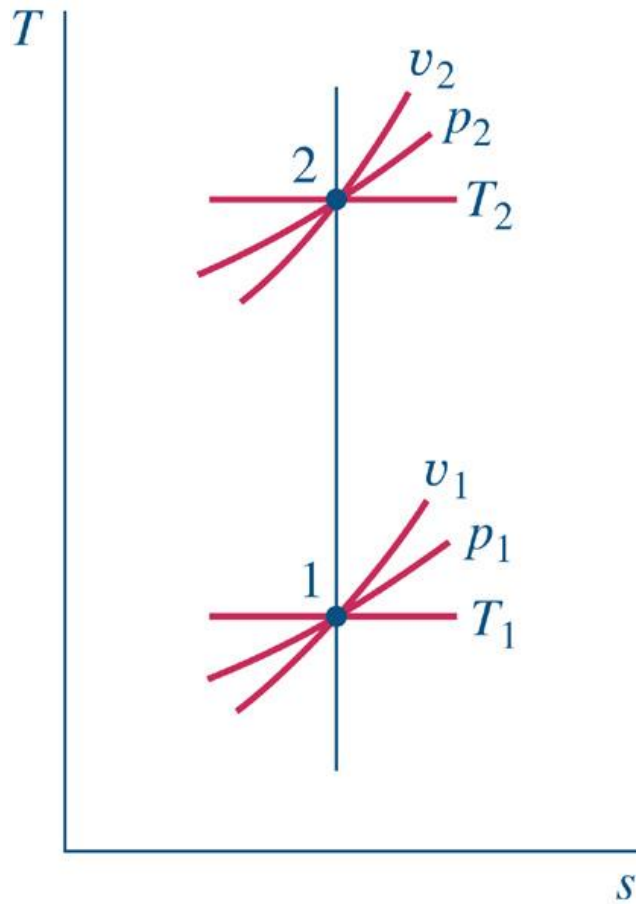
Taxa de
geração de
entropia

$$S_{VC}(t) = \int_{VC} \rho s dV$$

Processos Isentrópicos



Processos Isentrópicos: Modelo de Gás ideal



$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \left(\frac{p_2}{p_1} \right)$$

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \left(\frac{v_2}{v_1} \right)$$

$$0 = c_p \ln \frac{T_2}{T_1} - R \ln \left(\frac{p_2}{p_1} \right)$$

$$0 = c_v \ln \frac{T_2}{T_1} + R \ln \left(\frac{v_2}{v_1} \right)$$

Processos Isentrópicos: Modelo de Gás ideal

Da relação de gás ideal

$$c_p = \frac{kR}{k-1}$$

$$c_v = \frac{R}{k-1}$$

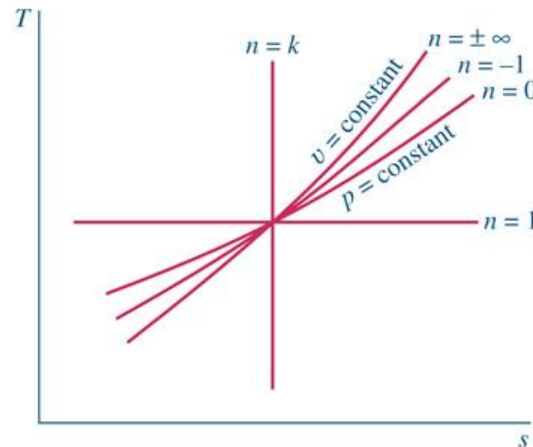
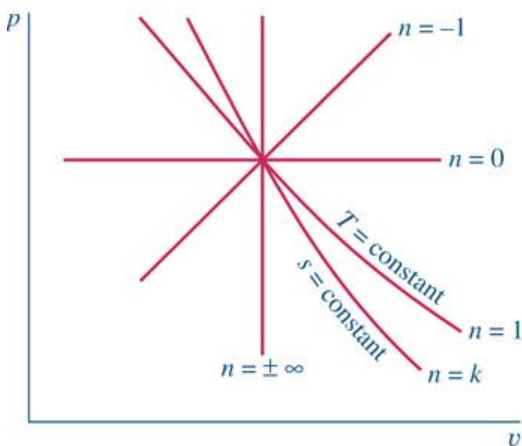
$$c_p - c_v = R$$

$$k = \frac{c_p}{c_v}$$

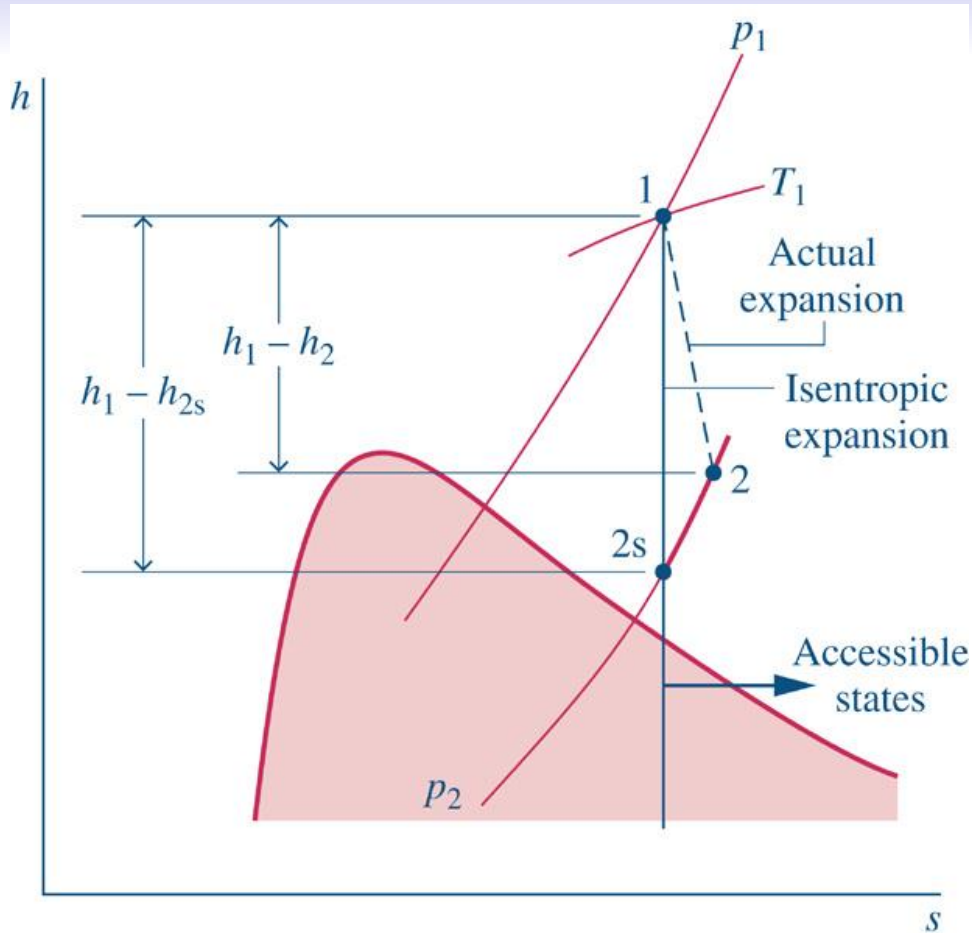
$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{(k-1)}{k}}$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{k-1}$$

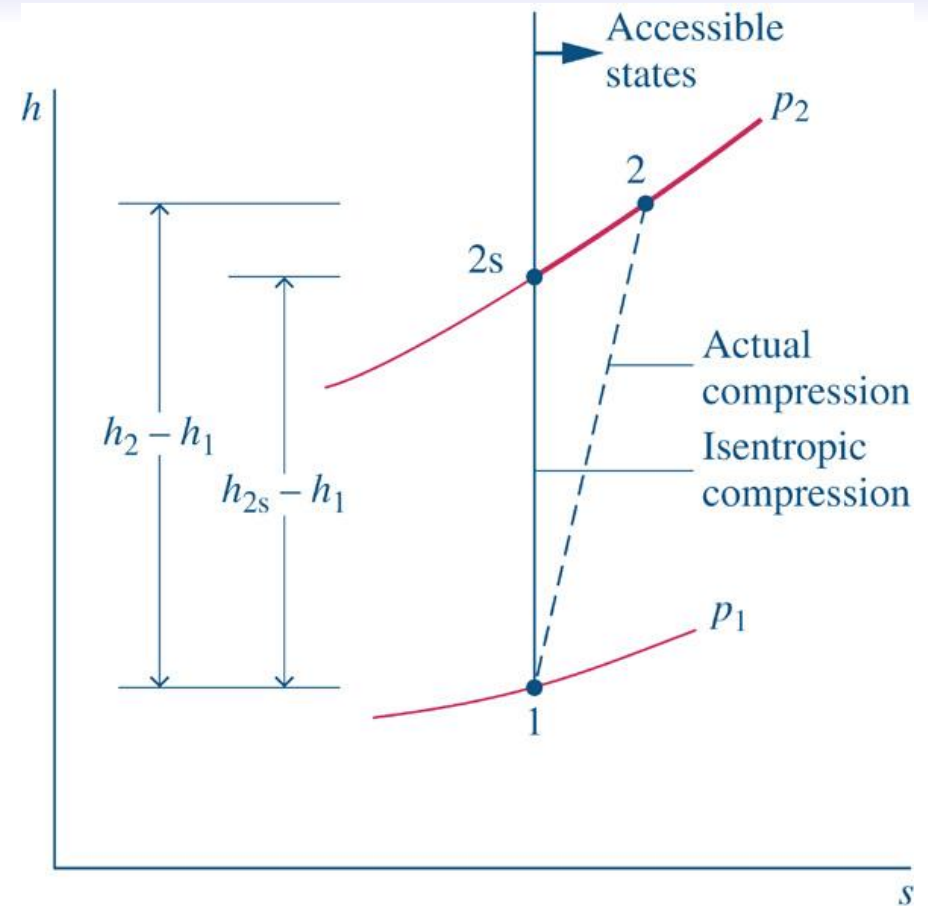
$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2} \right)^k$$



Eficiência Isentrópica



$$\eta_t = \frac{\dot{W}_{VC}/\dot{m}}{(\dot{W}_{VC}/\dot{m})_s} = \frac{h_1 - h_2}{h_1 - h_{2s}}$$



$$\eta_c = \frac{(\dot{W}_{VC}/\dot{m})_s}{\dot{W}_{VC}/\dot{m}} = \frac{h_{2s} - h_1}{h_2 - h_1}$$

Ex. 6.6: Geração de Entropia em uma Turbina a Vapor

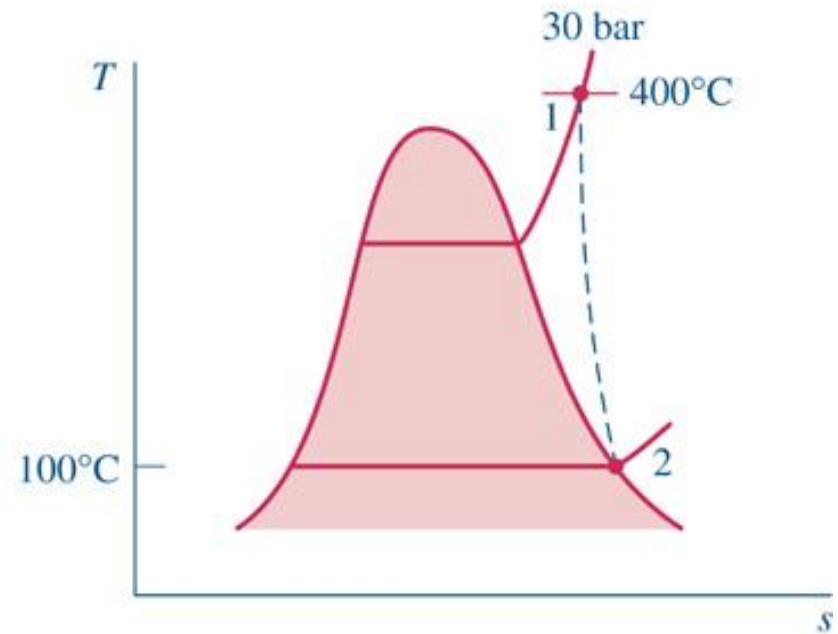
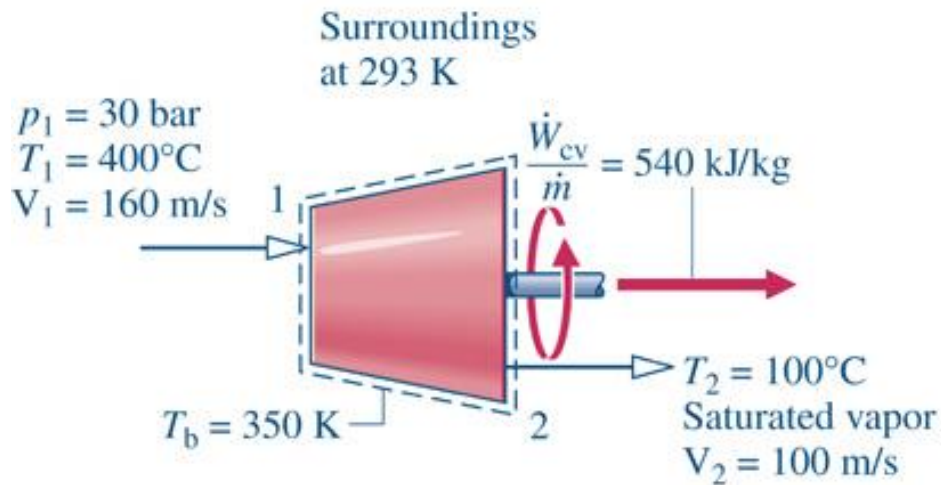


Fig06_12

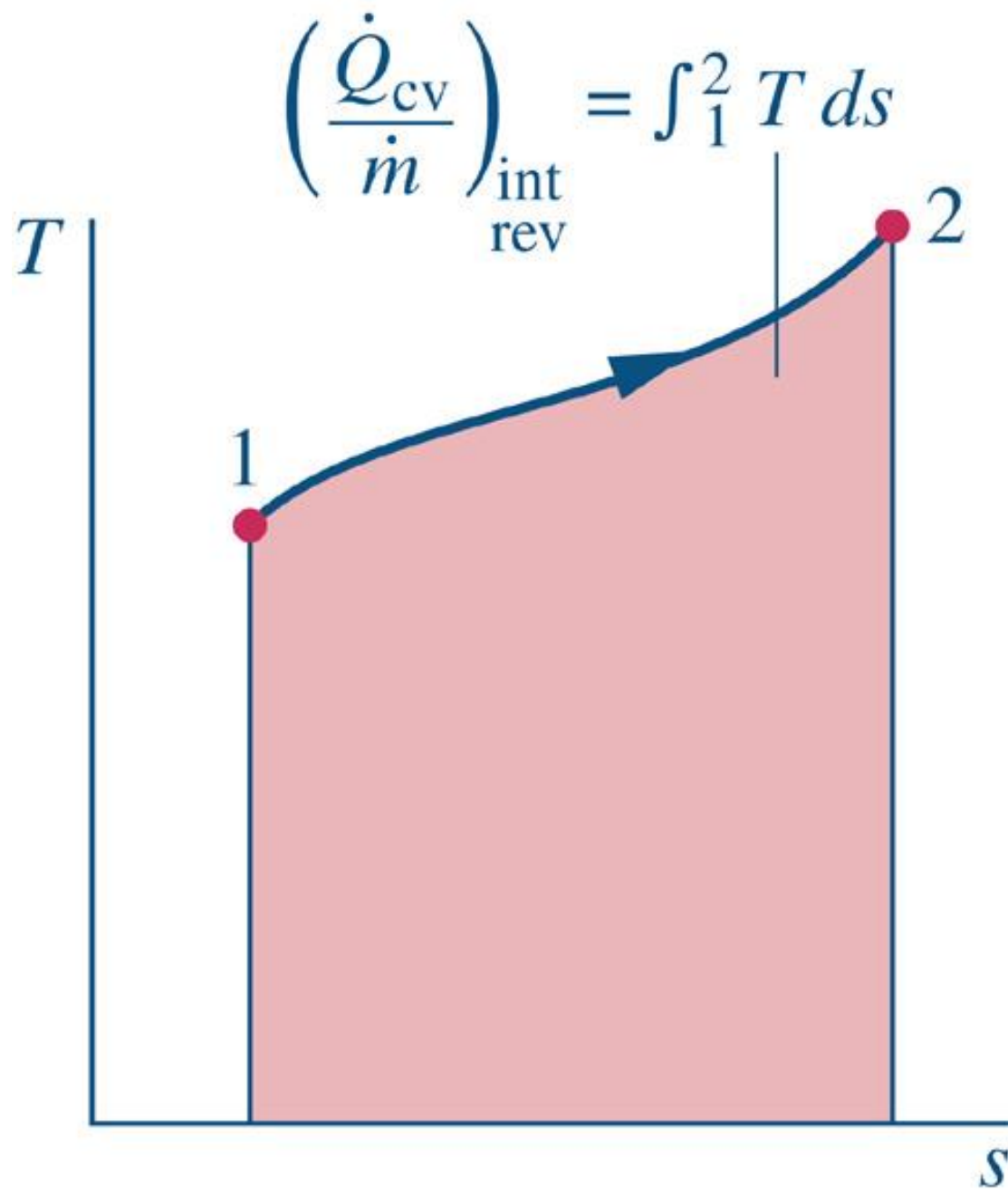


Fig06_13

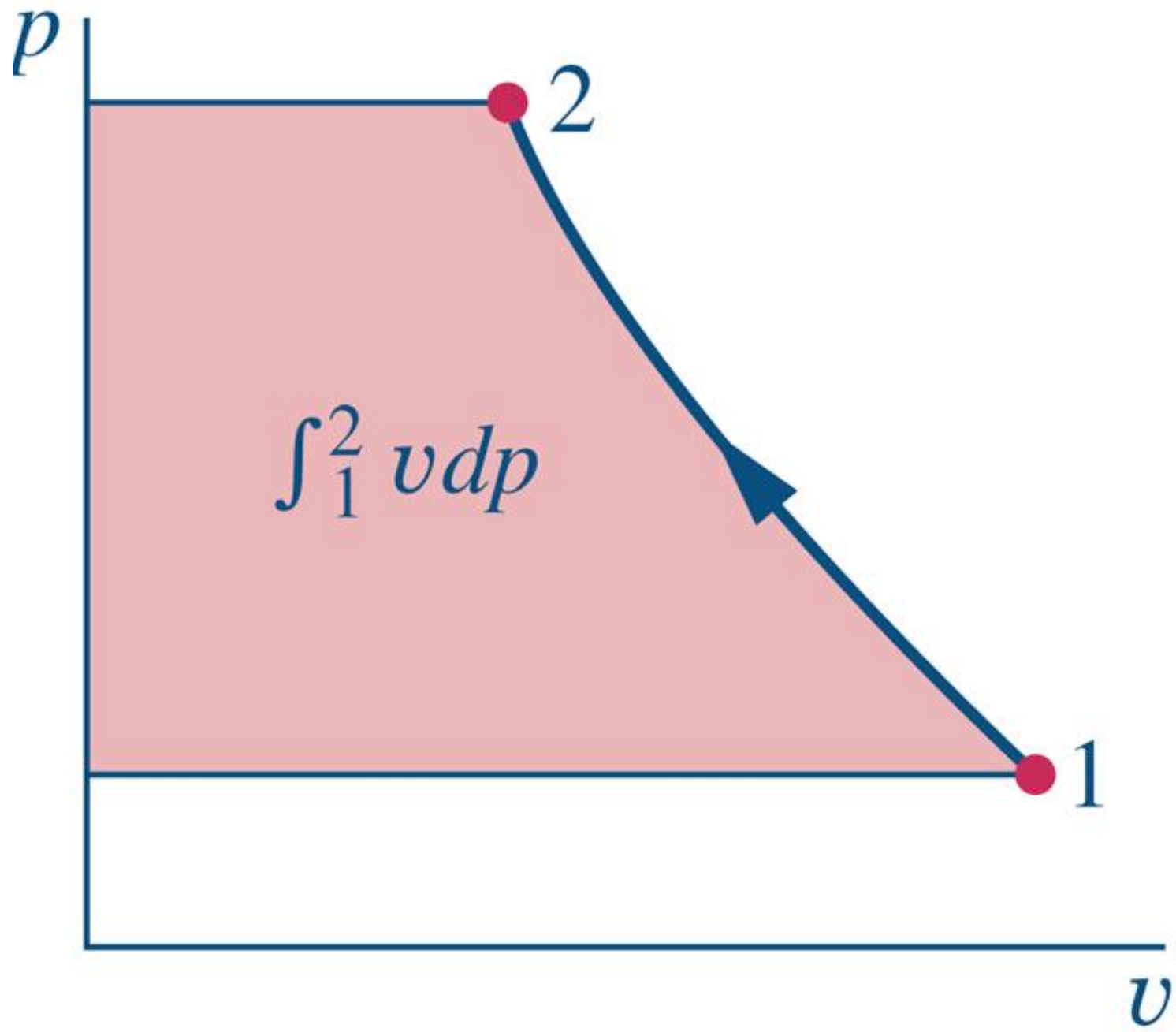


Fig06_14

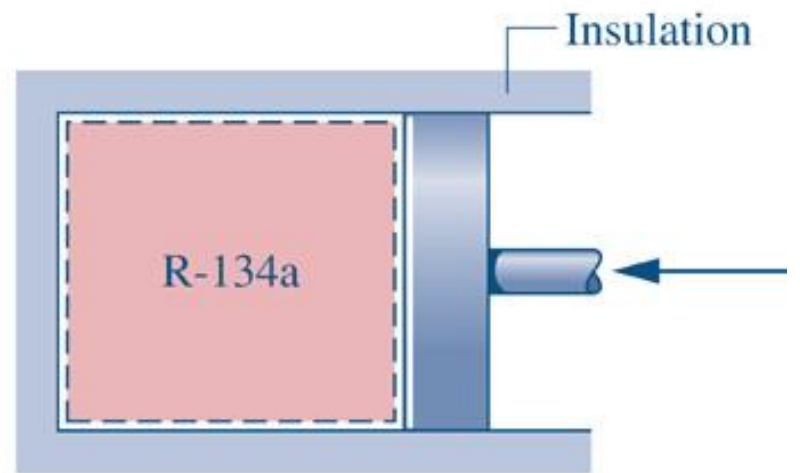
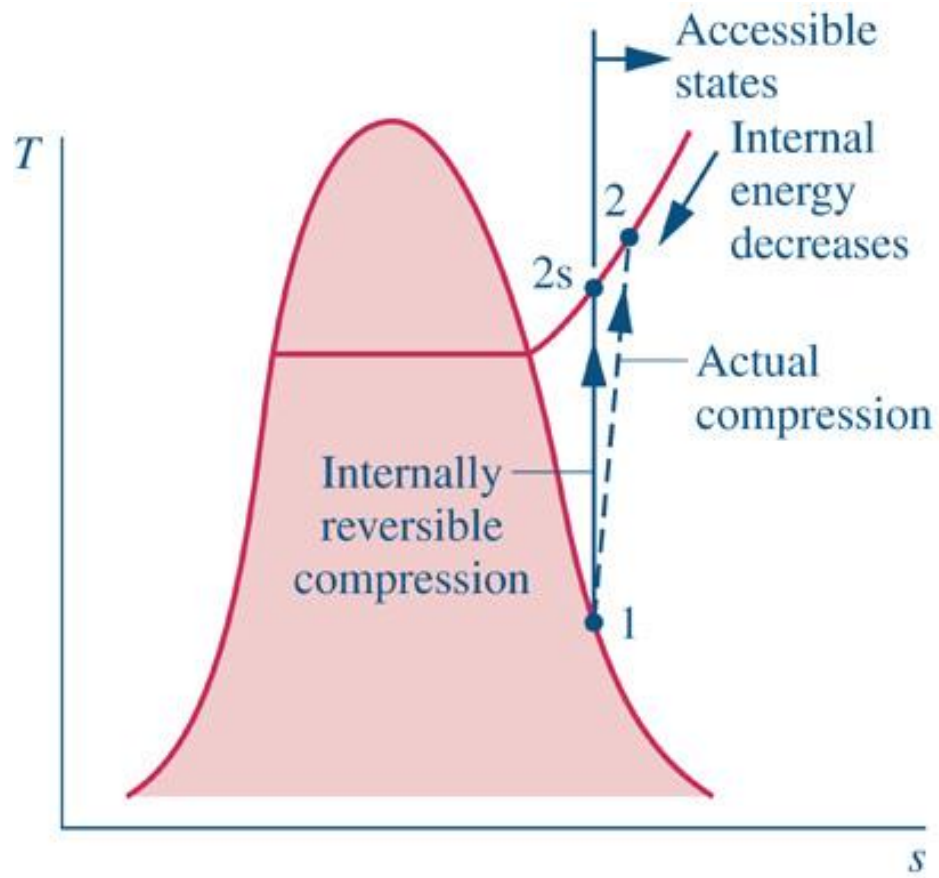


Fig06_E6

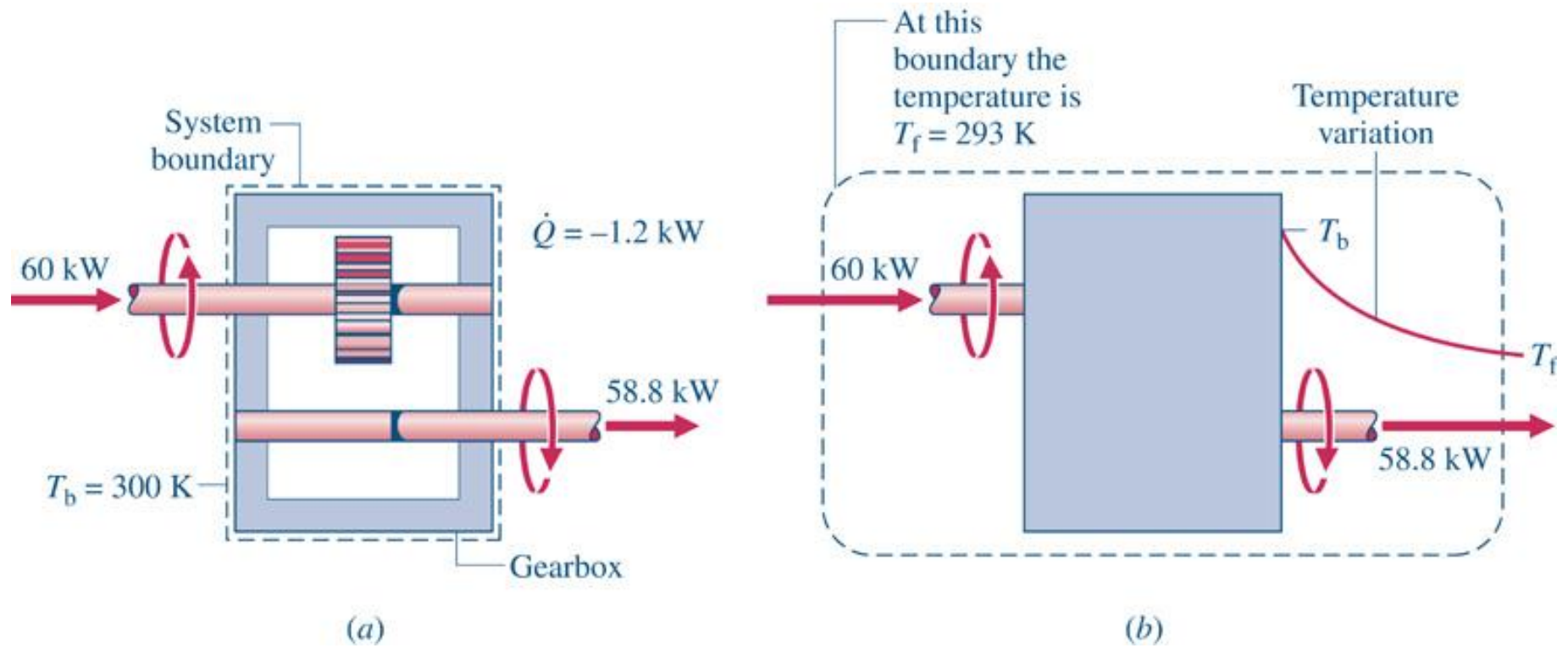
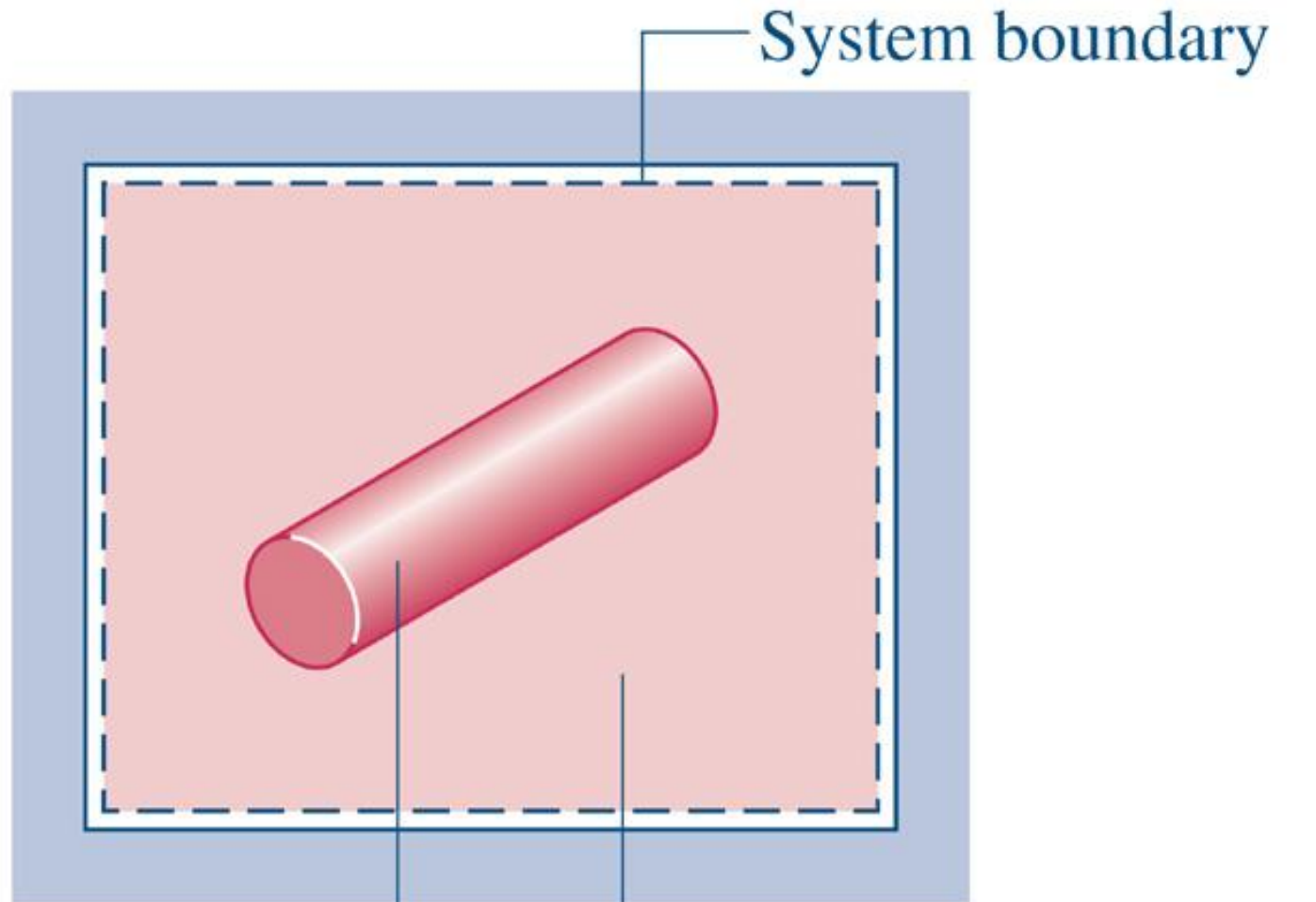


Fig06_E6



Metal bar:

$$T_{mi} = 1900^{\circ}\text{R}$$

$$c_m = 0.1 \text{ Btu/lb}\cdot^{\circ}\text{R}$$

$$m_m = 0.8 \text{ lb}$$

Water:

$$T_{wi} = 530^{\circ}\text{R}$$

$$c_w = 1.0 \text{ Btu/lb}\cdot^{\circ}\text{R}$$

$$m_w = 20 \text{ lb}$$

Fig06_E6

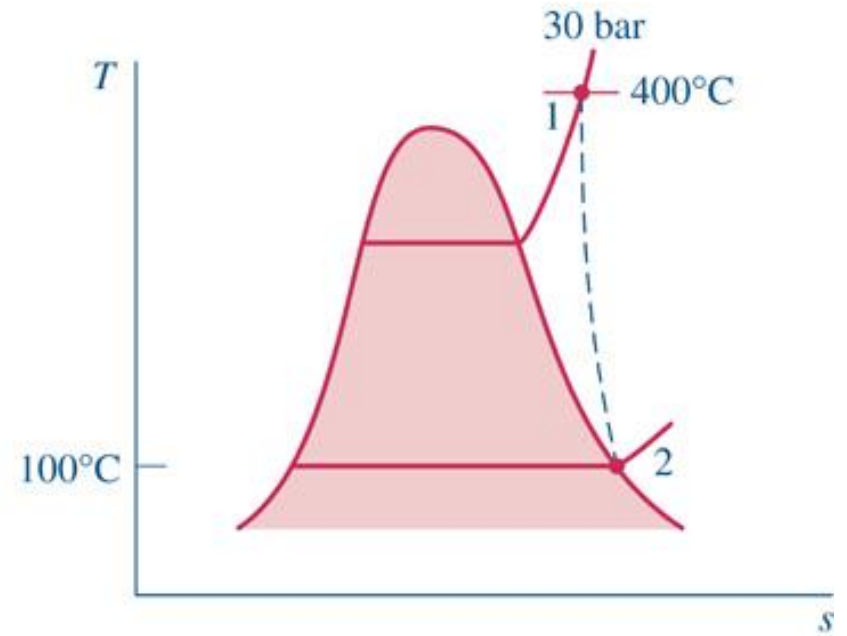
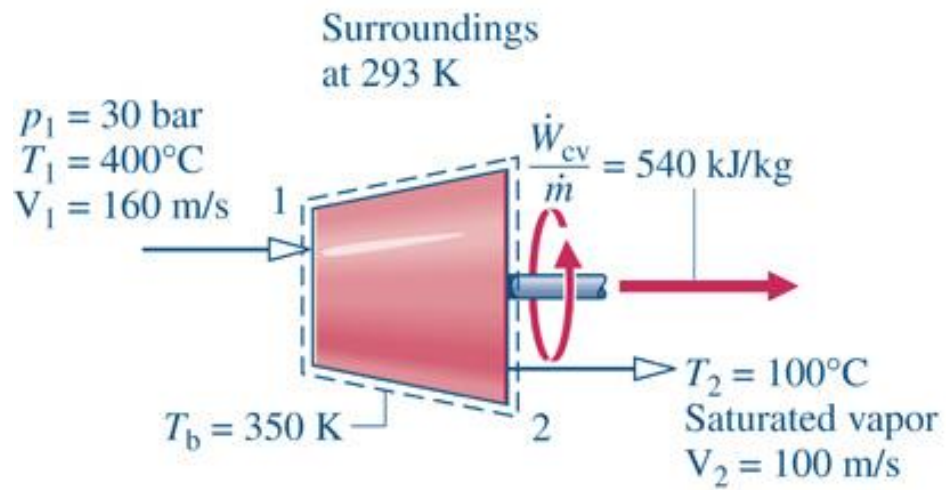


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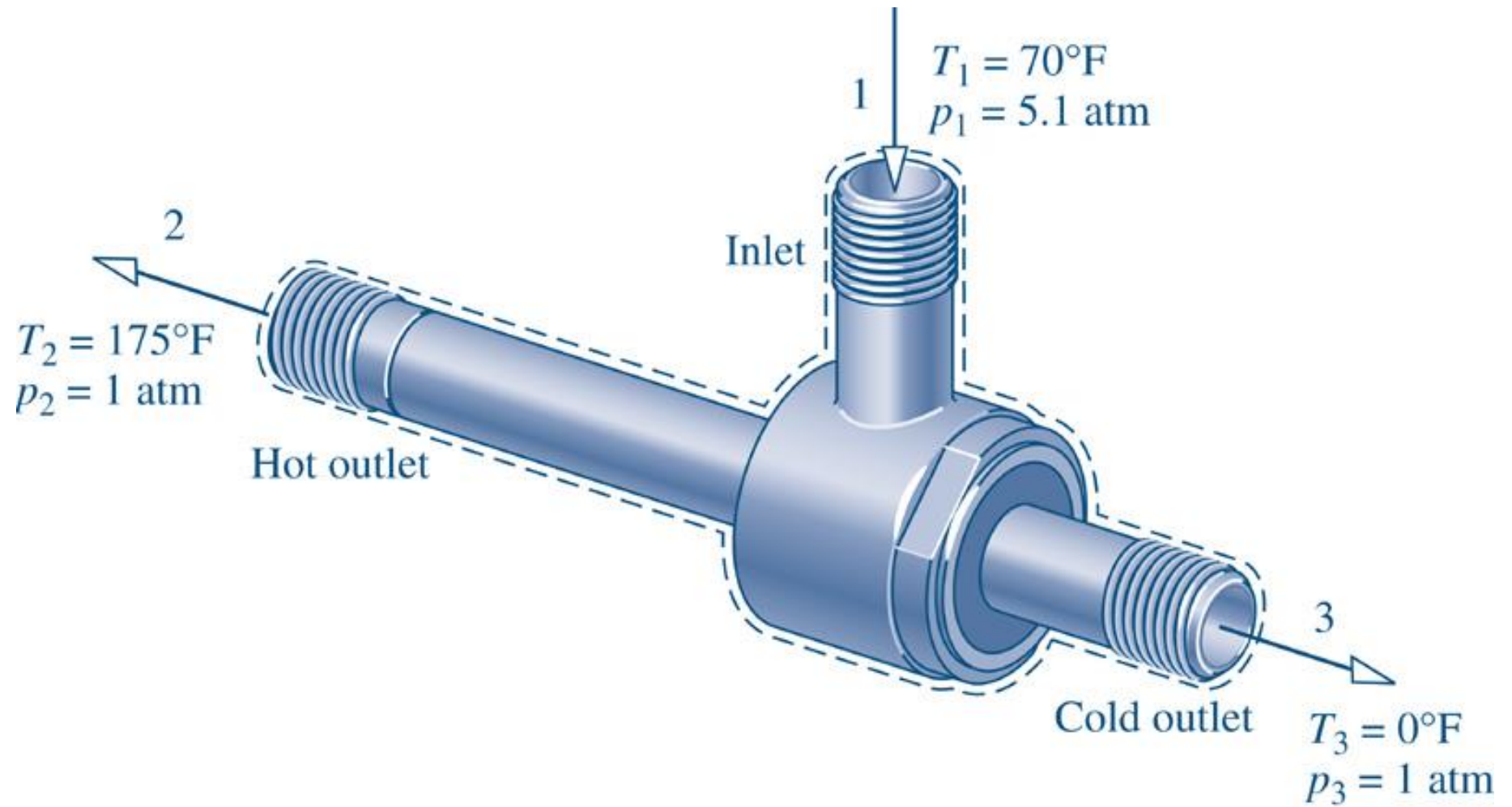


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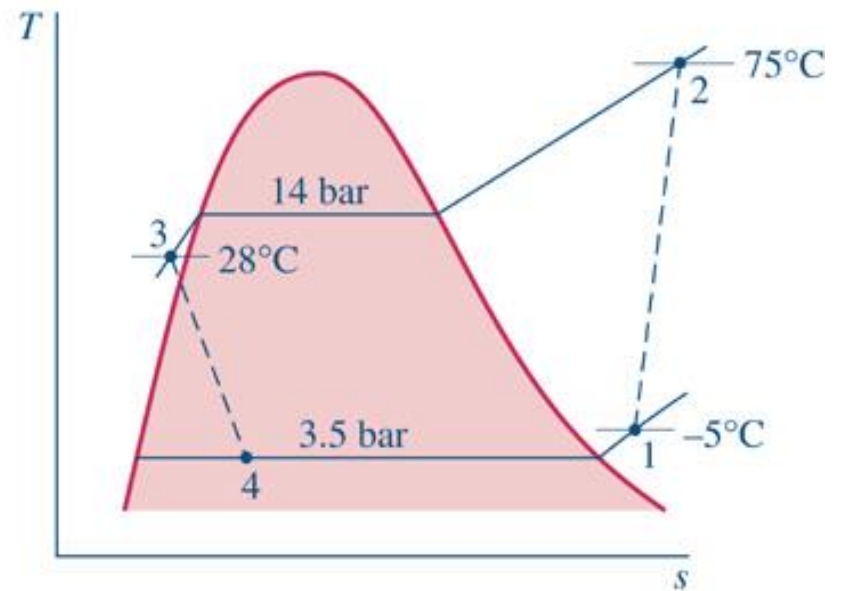
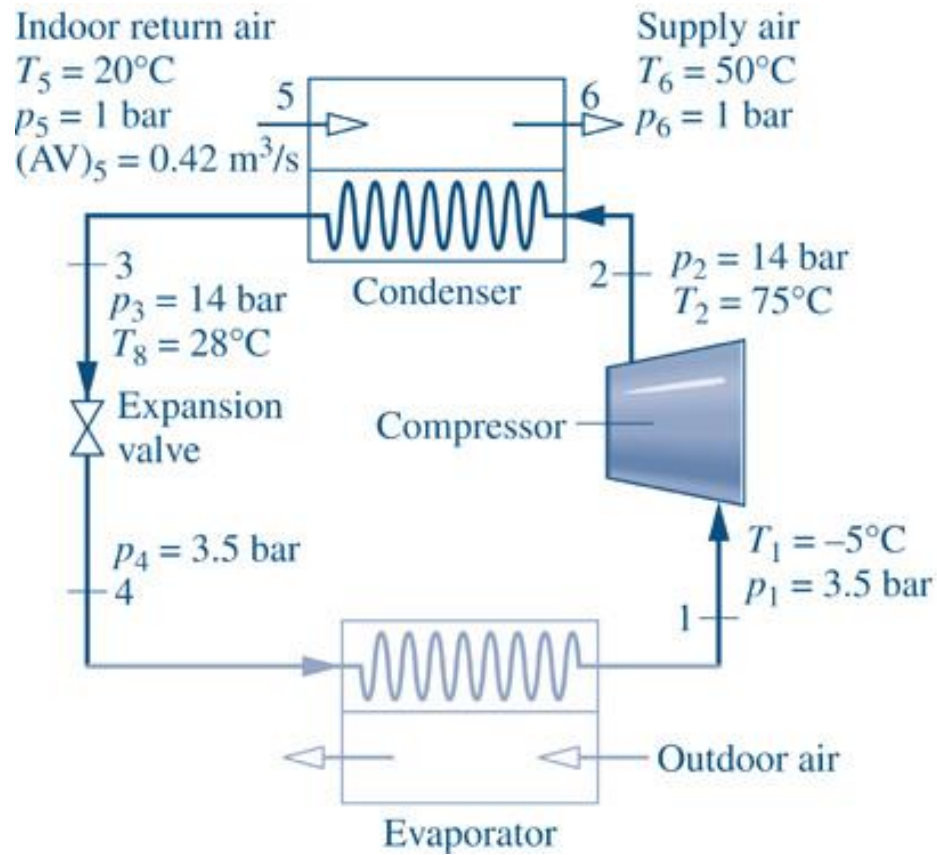


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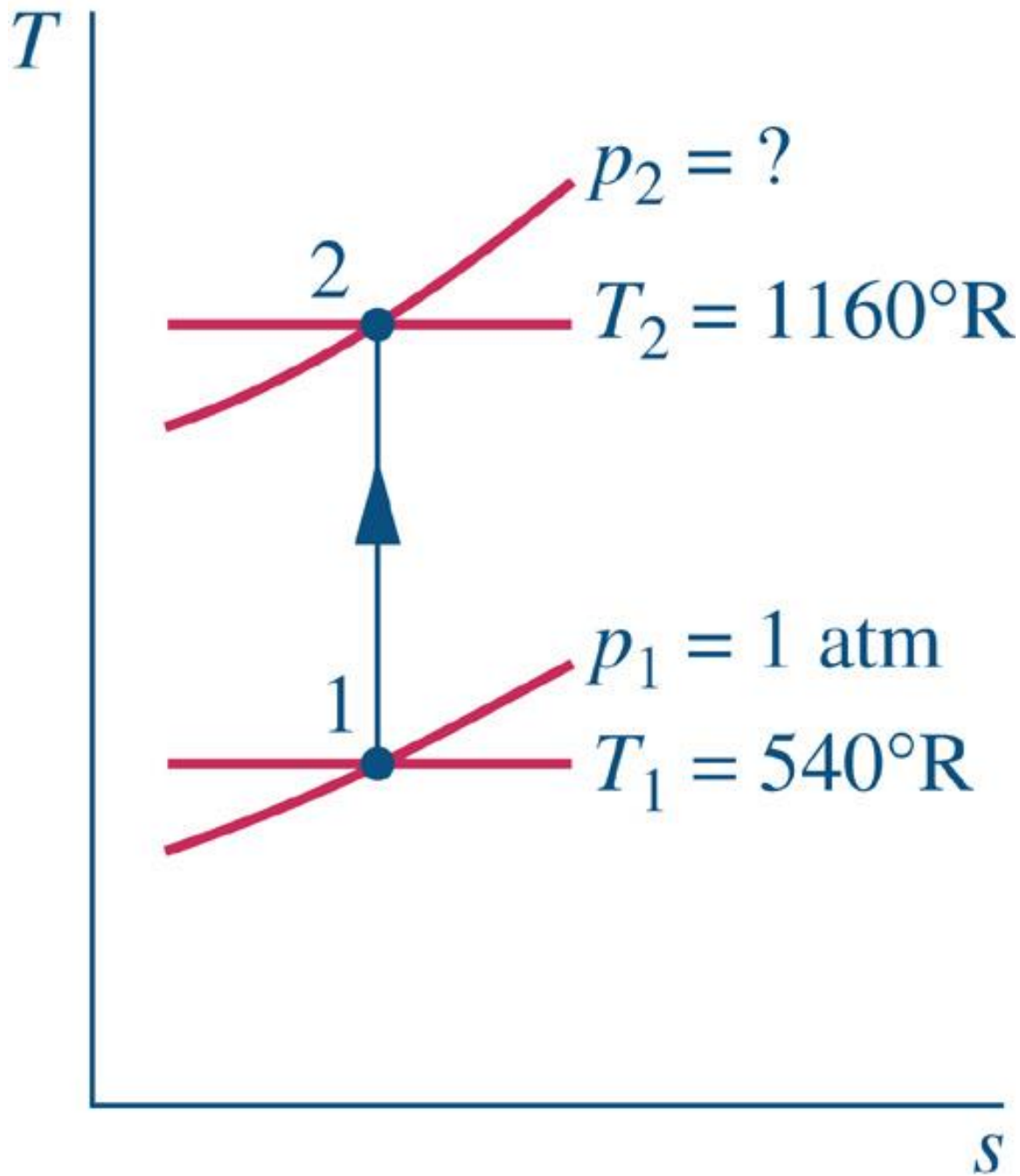
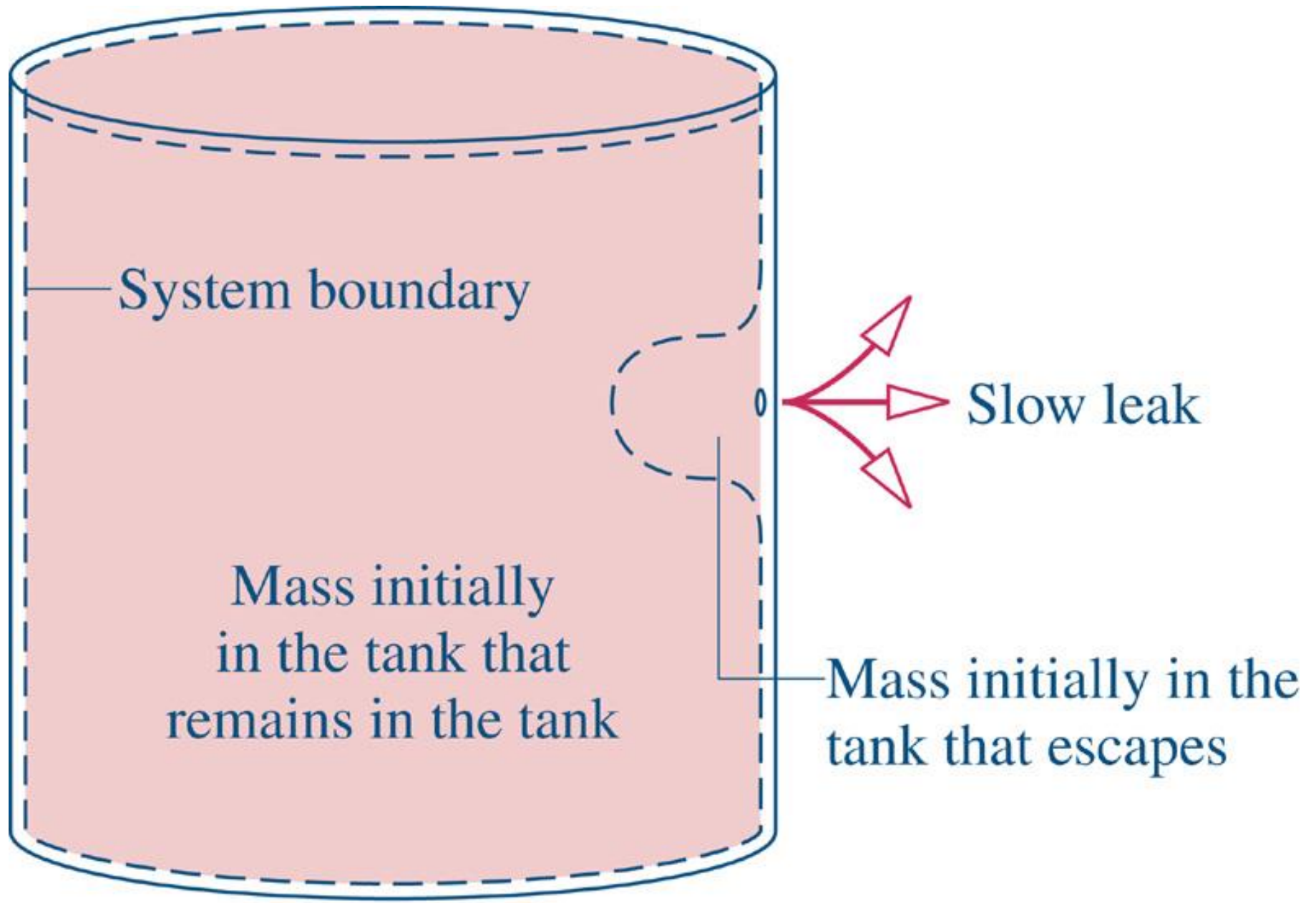


Fig06_E6



Initial condition of tank

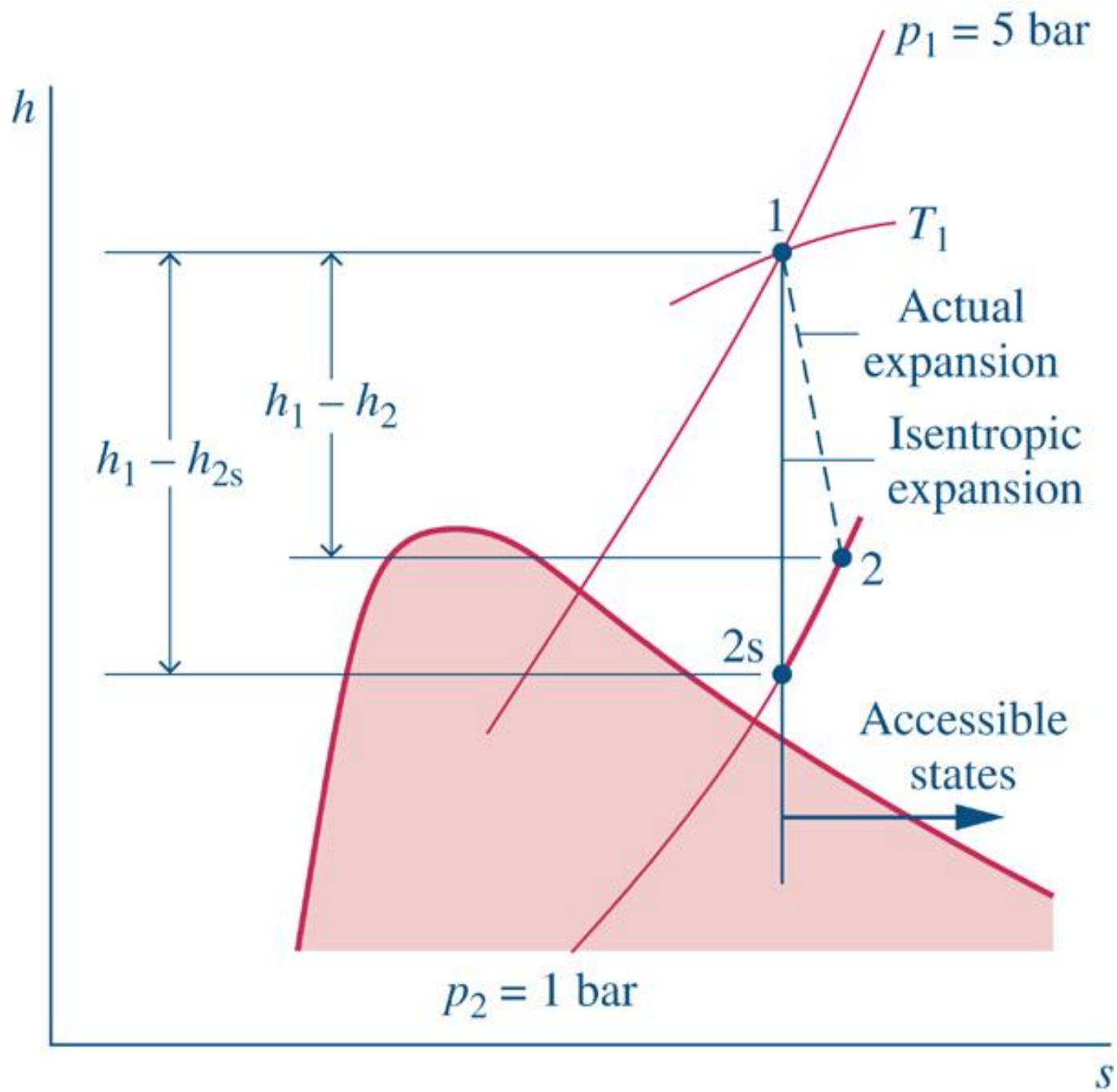


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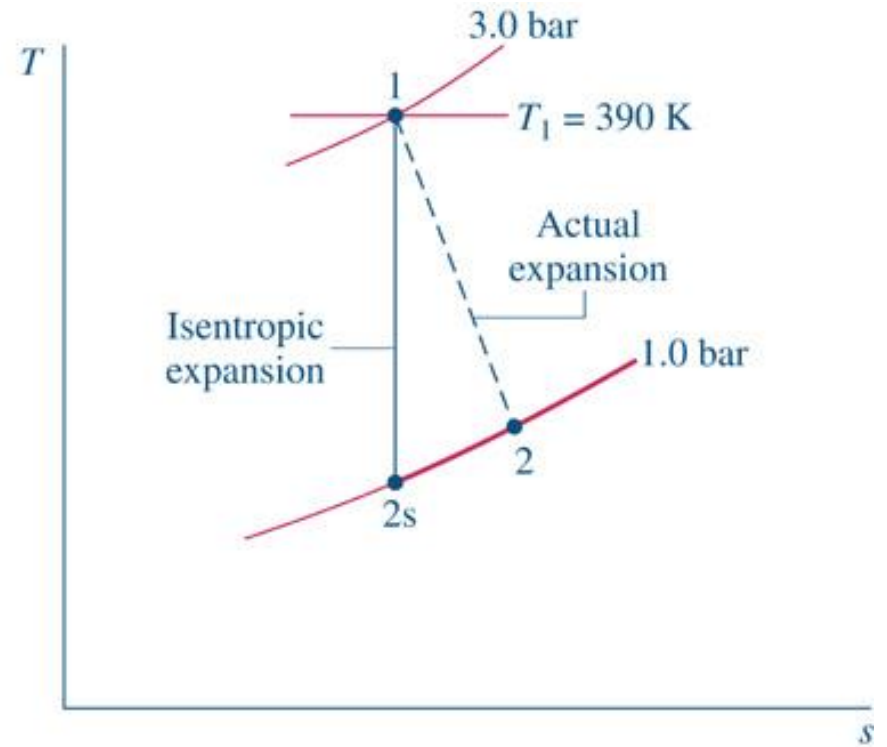
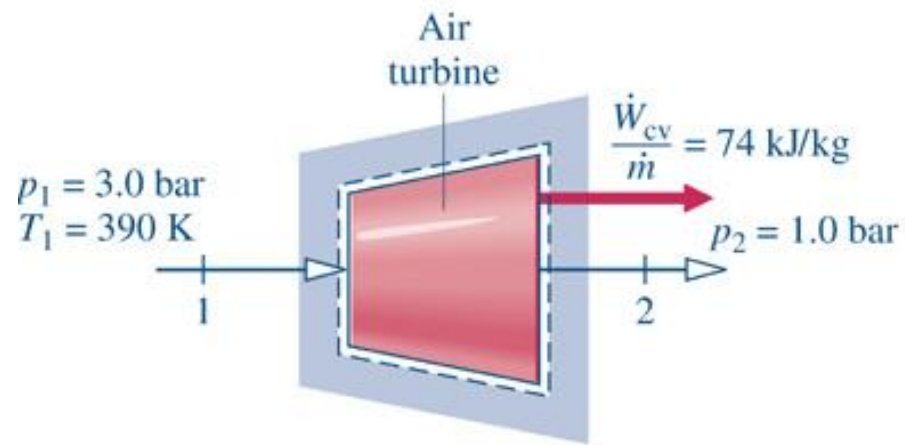


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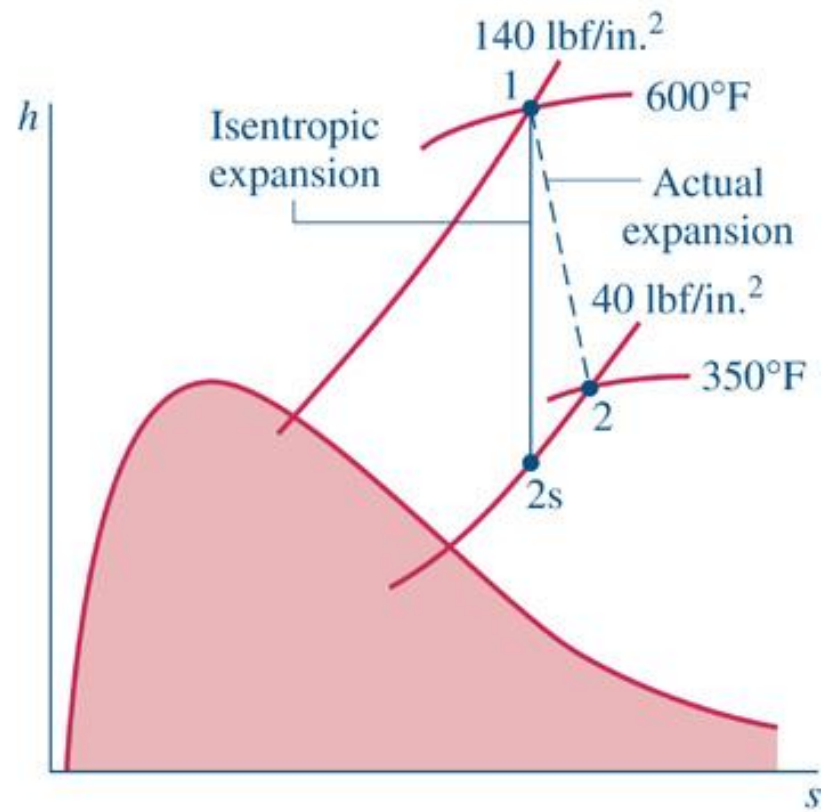
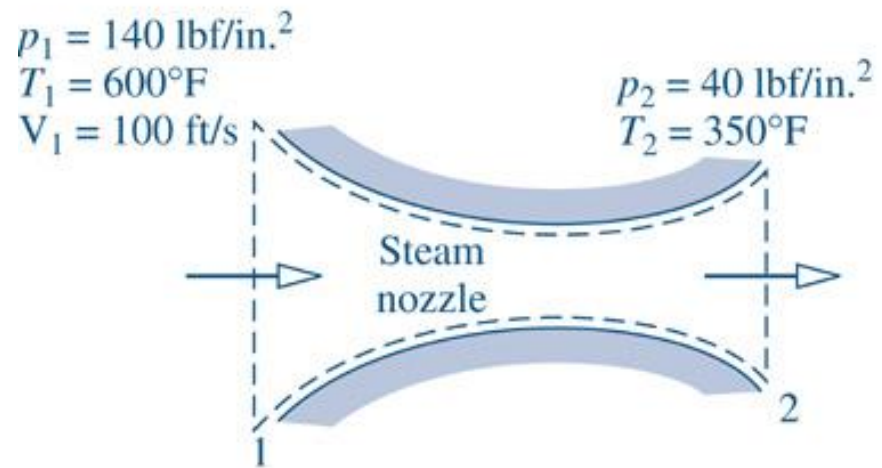


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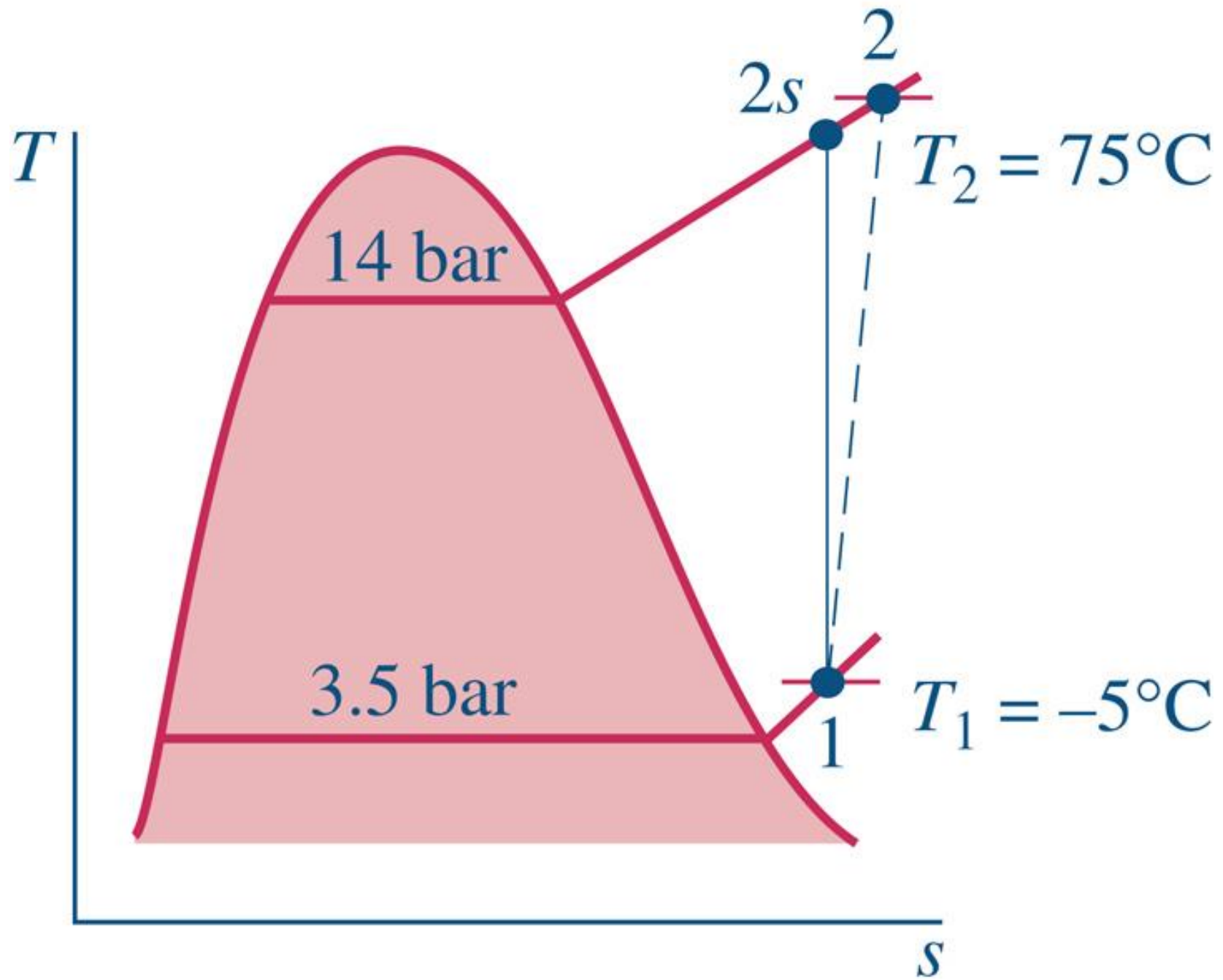


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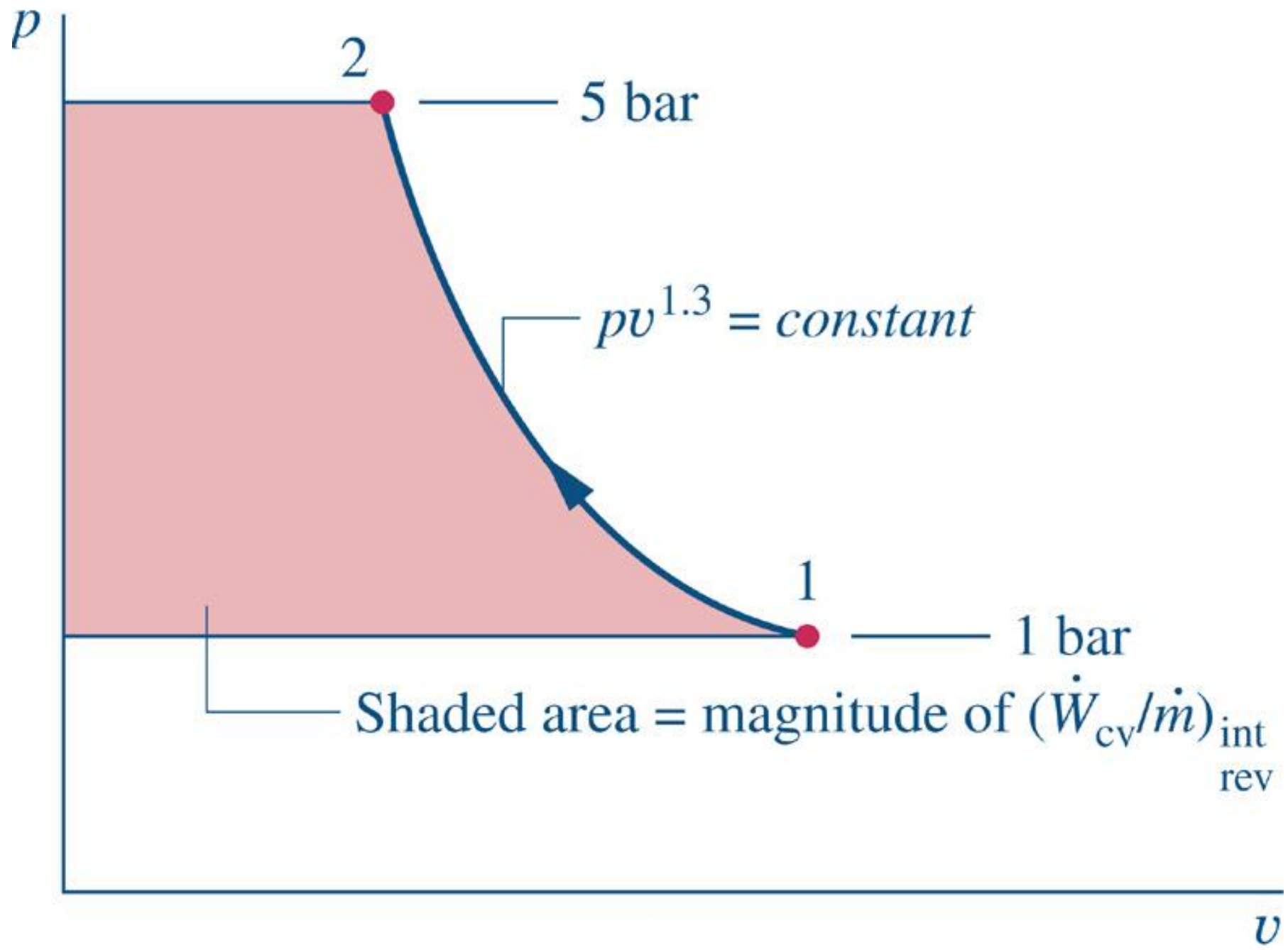


Fig06_E6

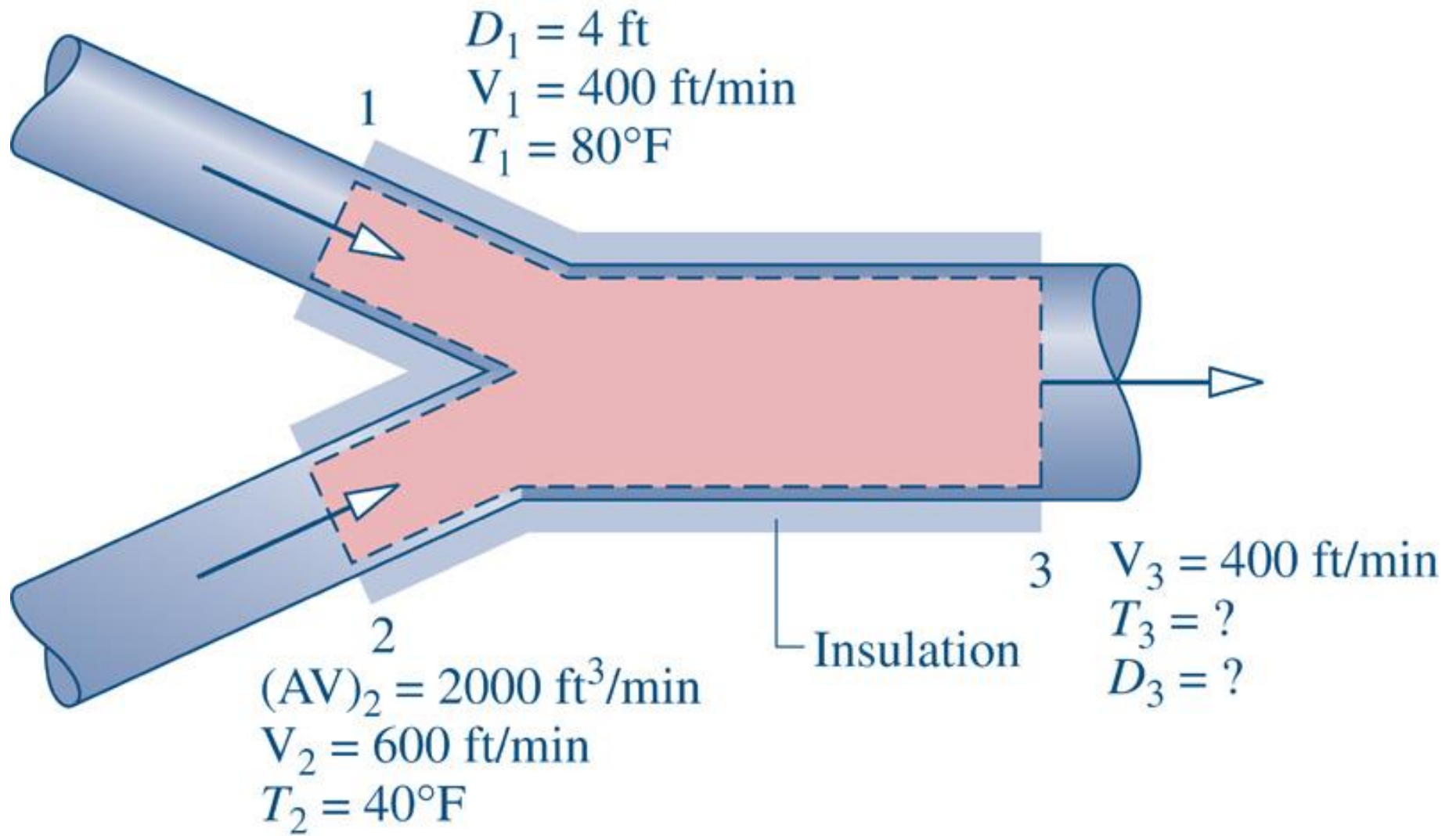


Fig06_P6

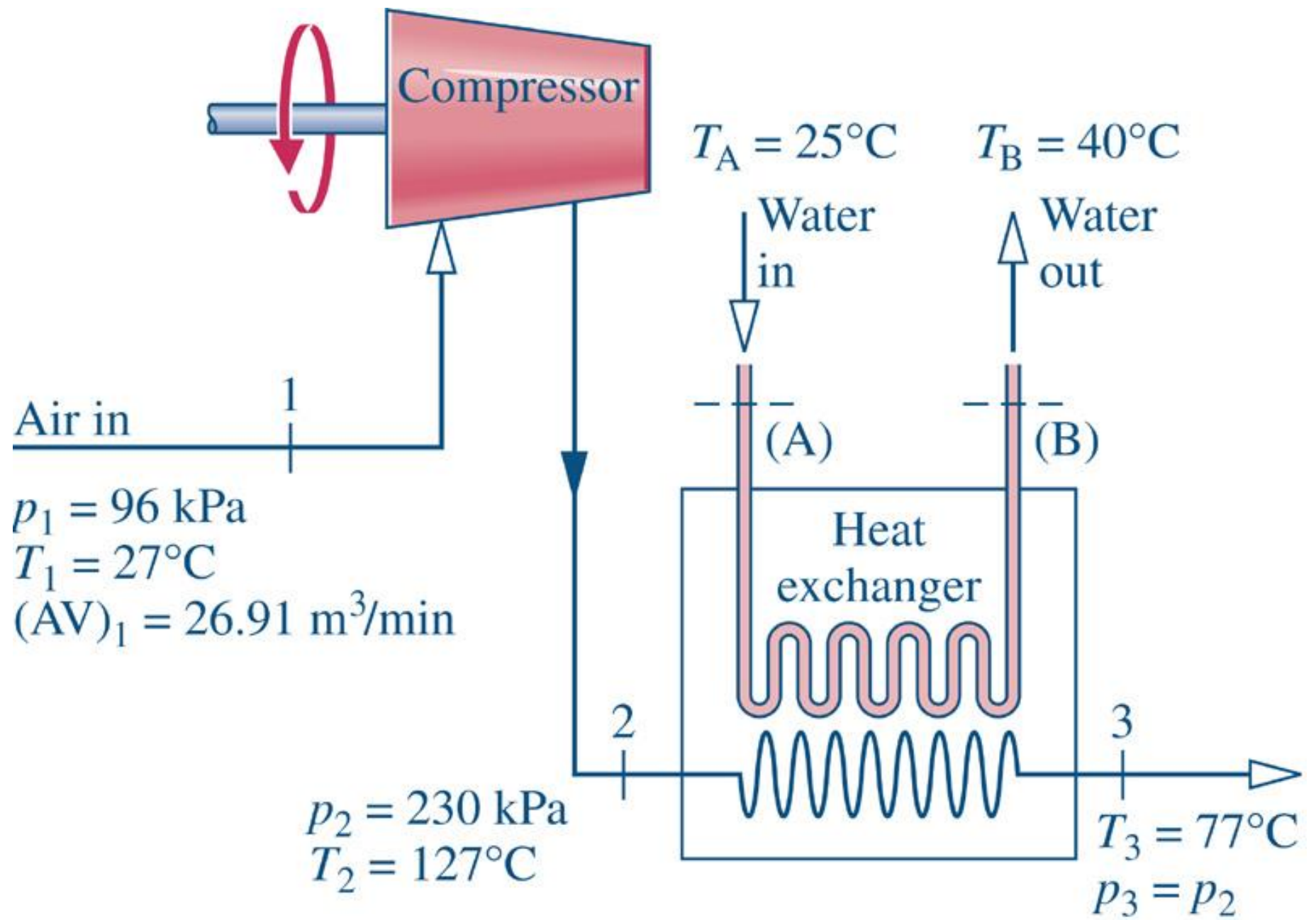


Fig06_P6

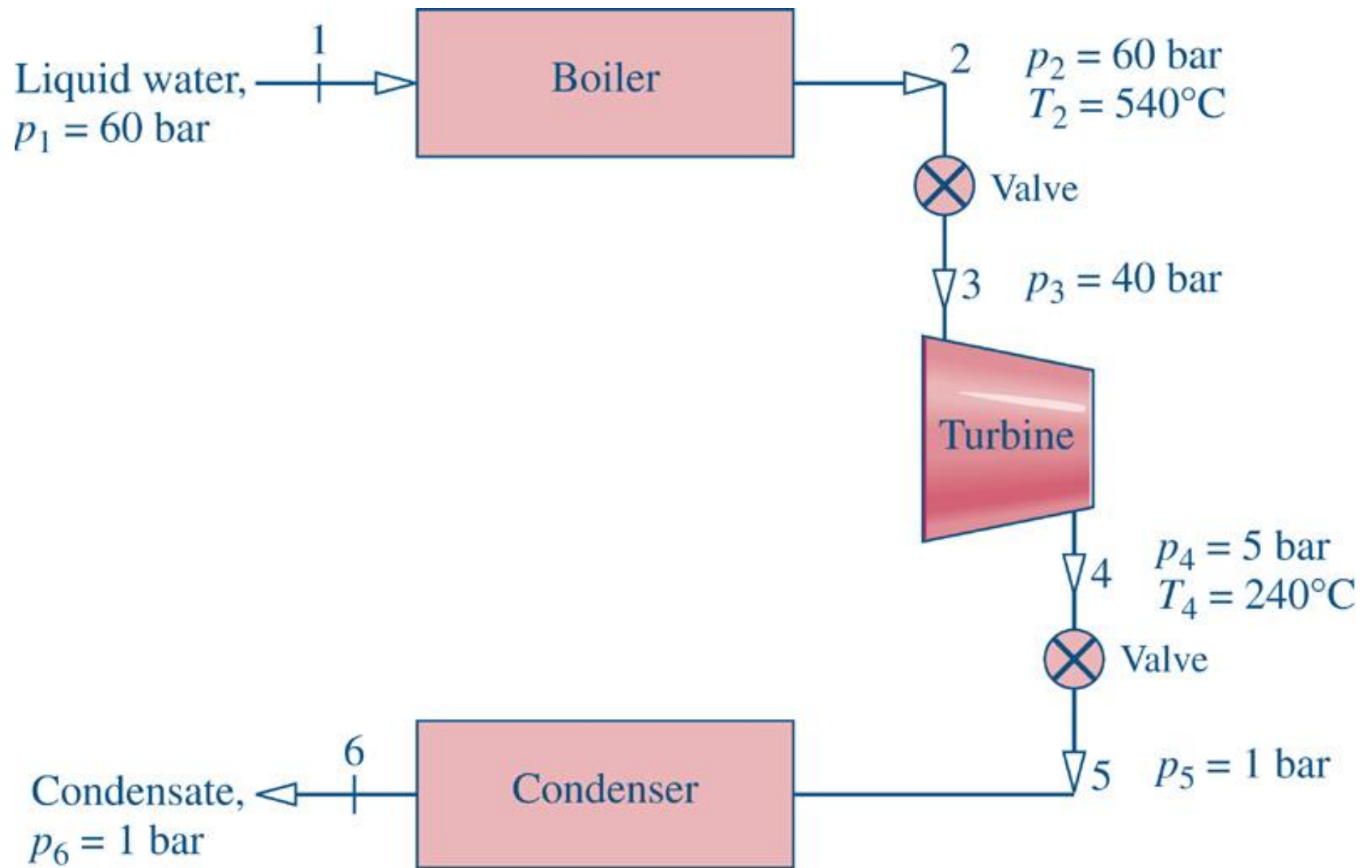


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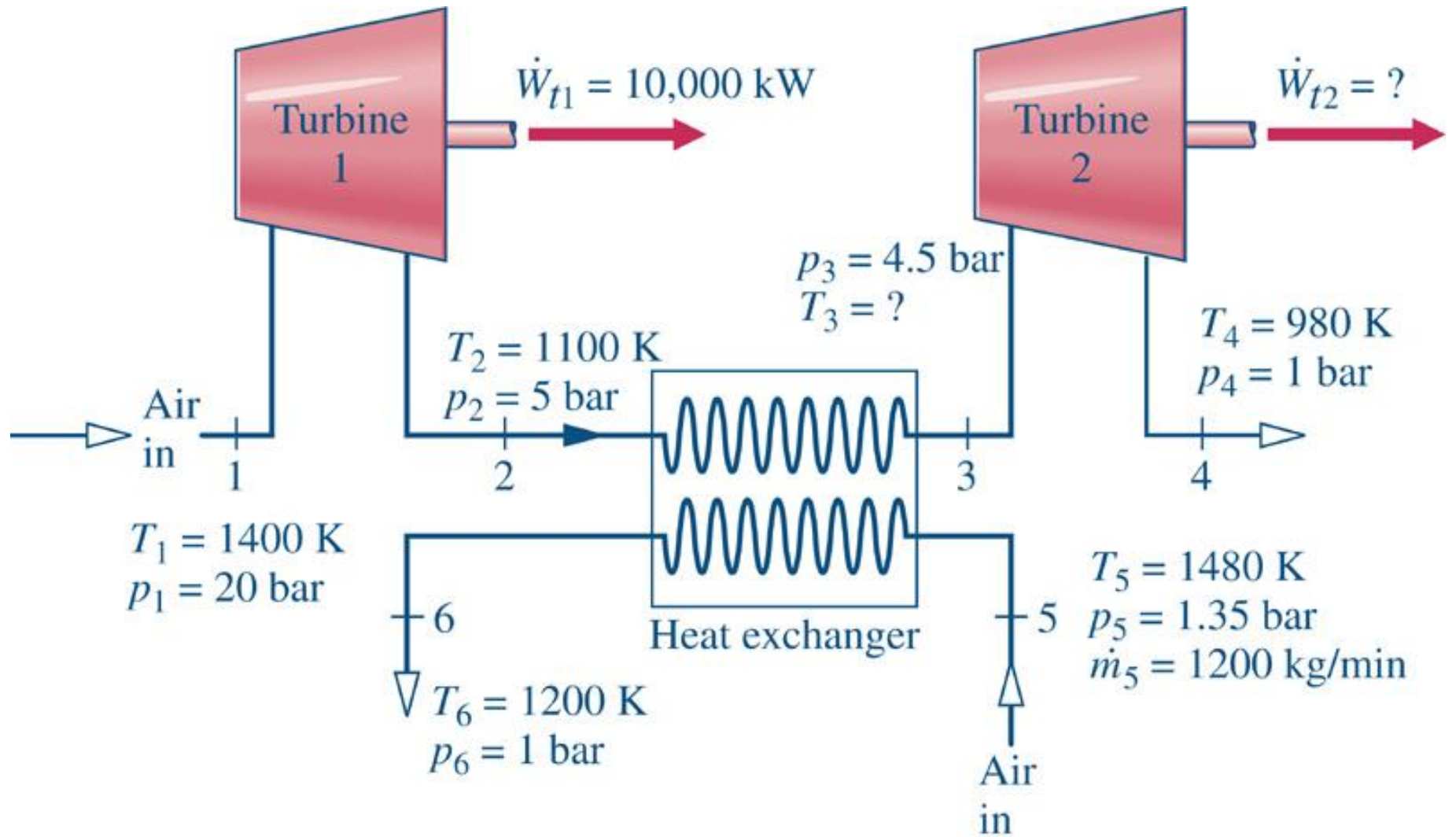


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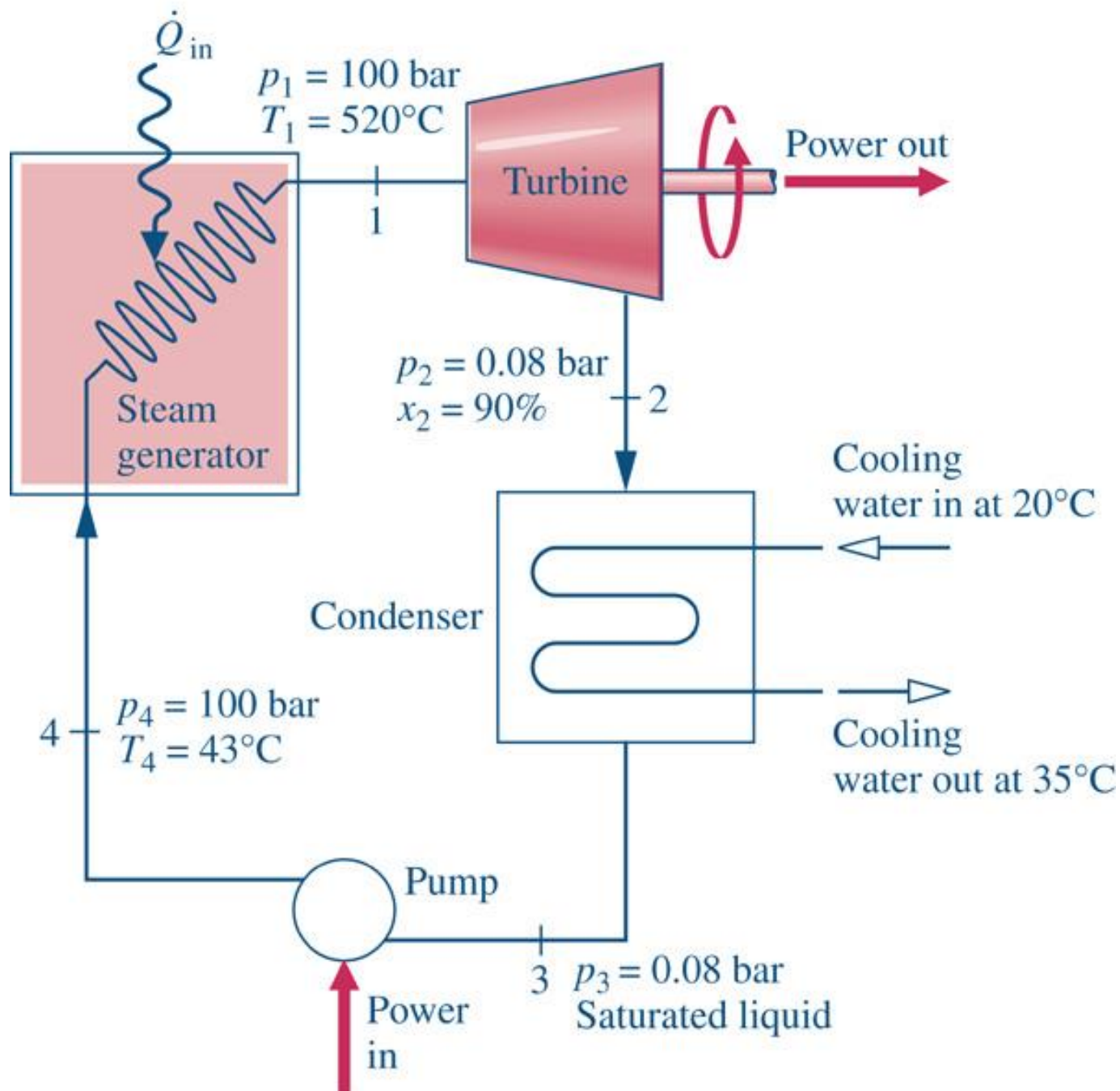


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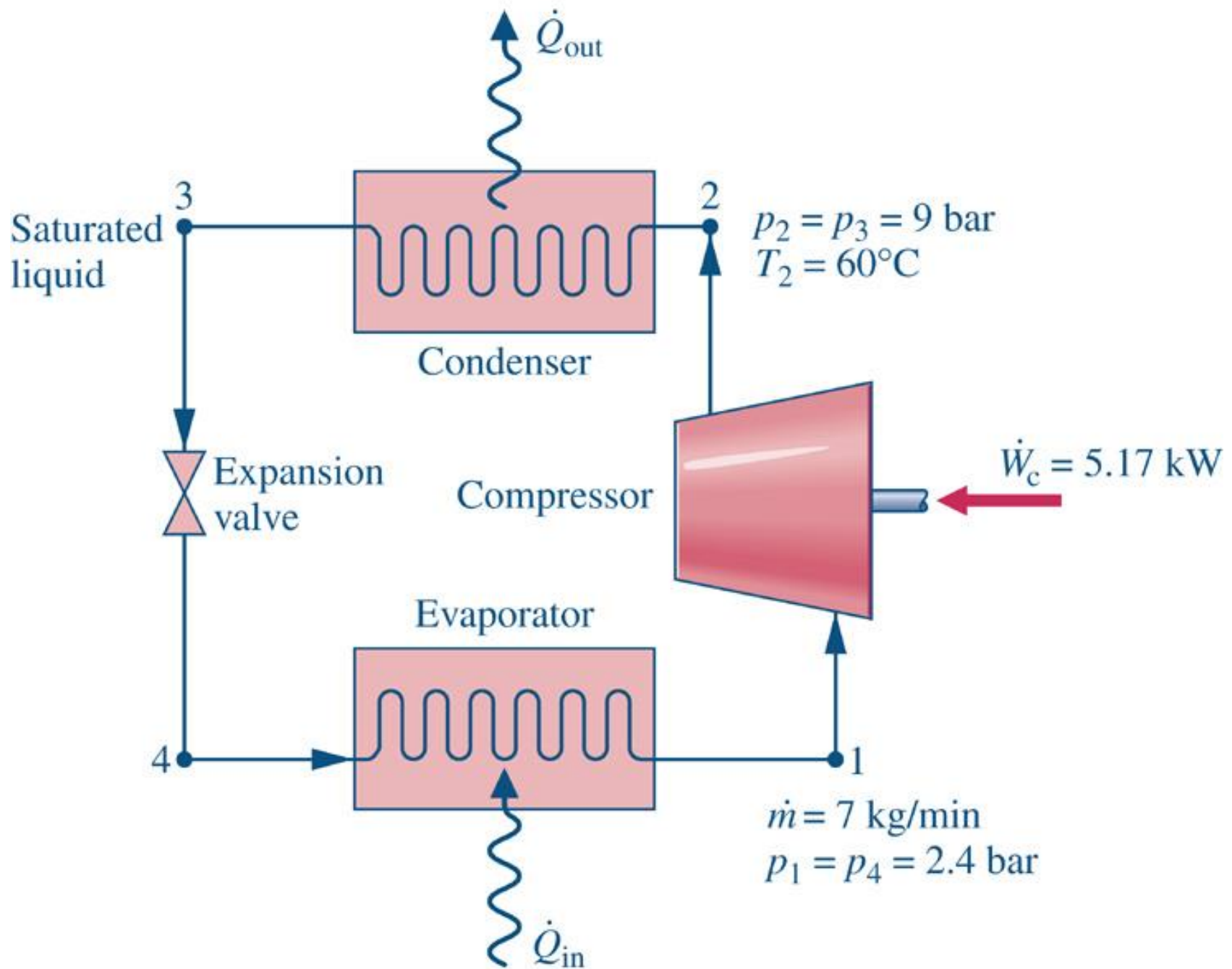


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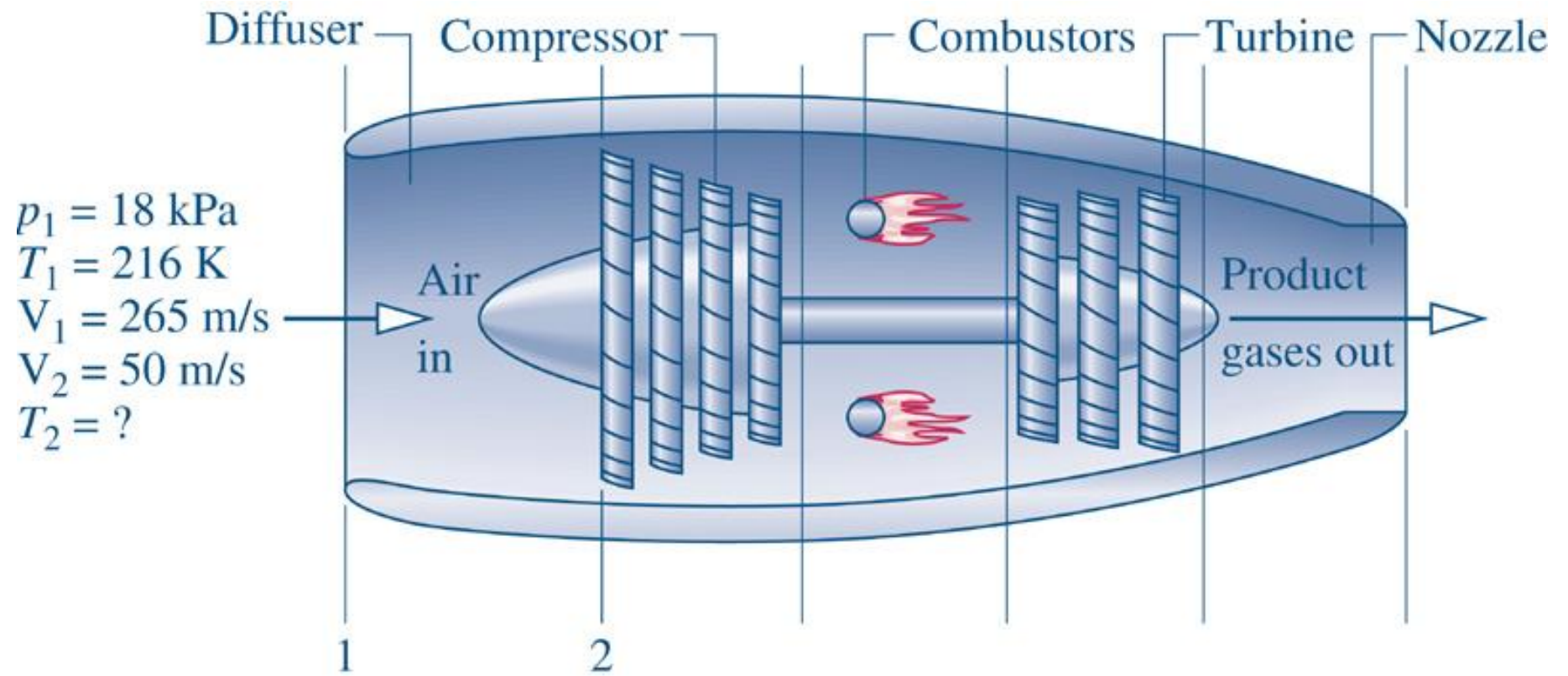


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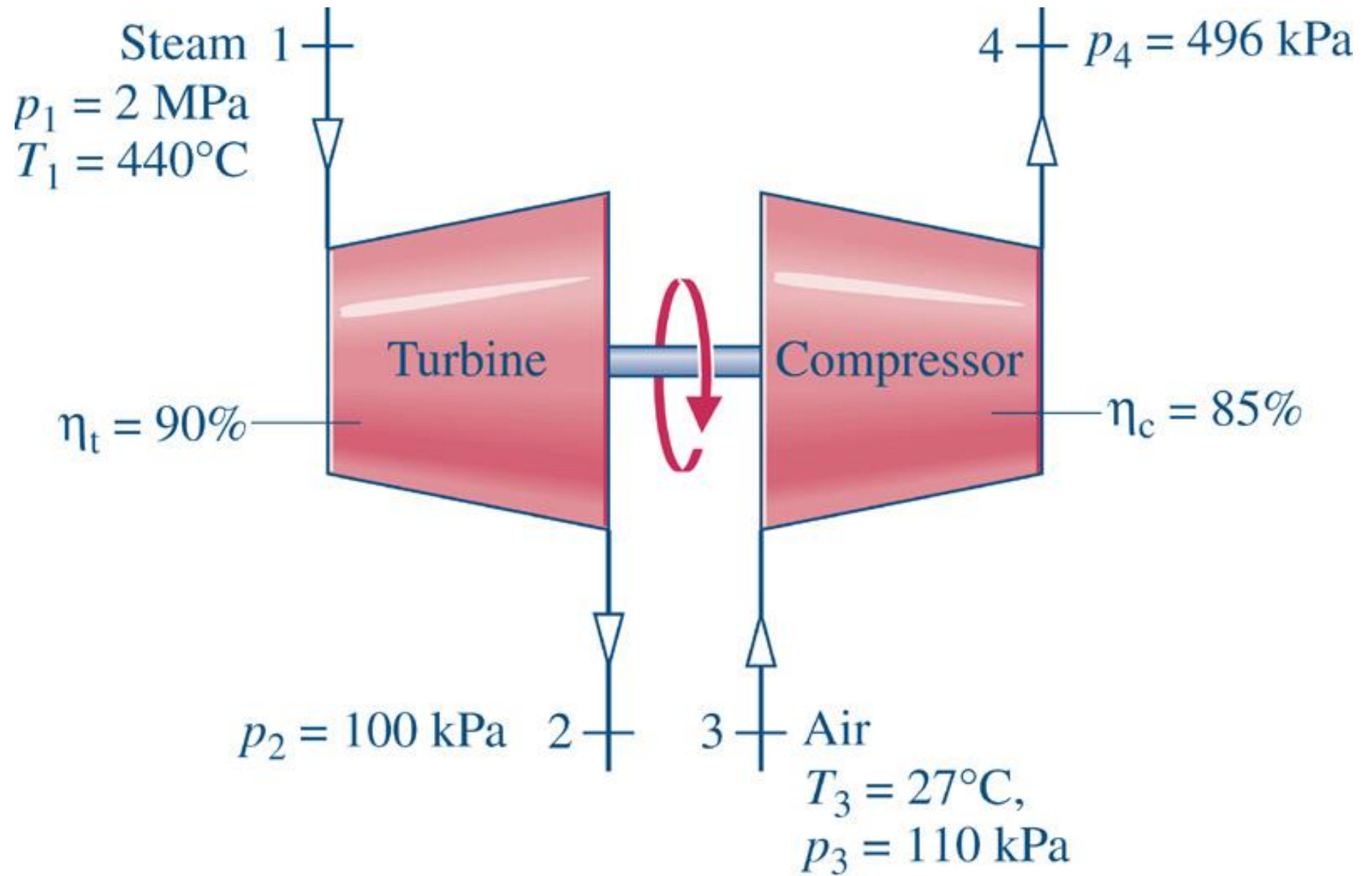


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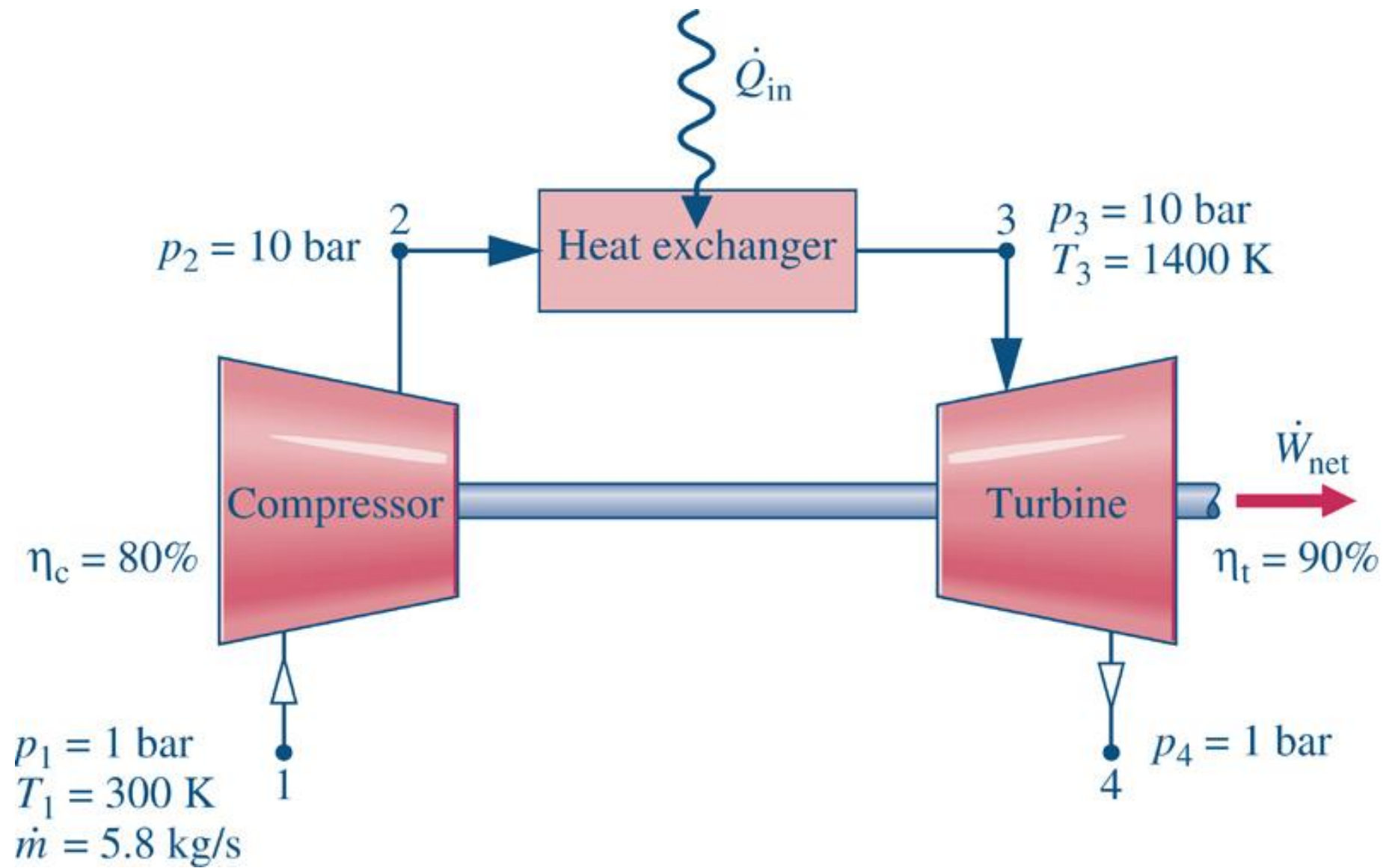


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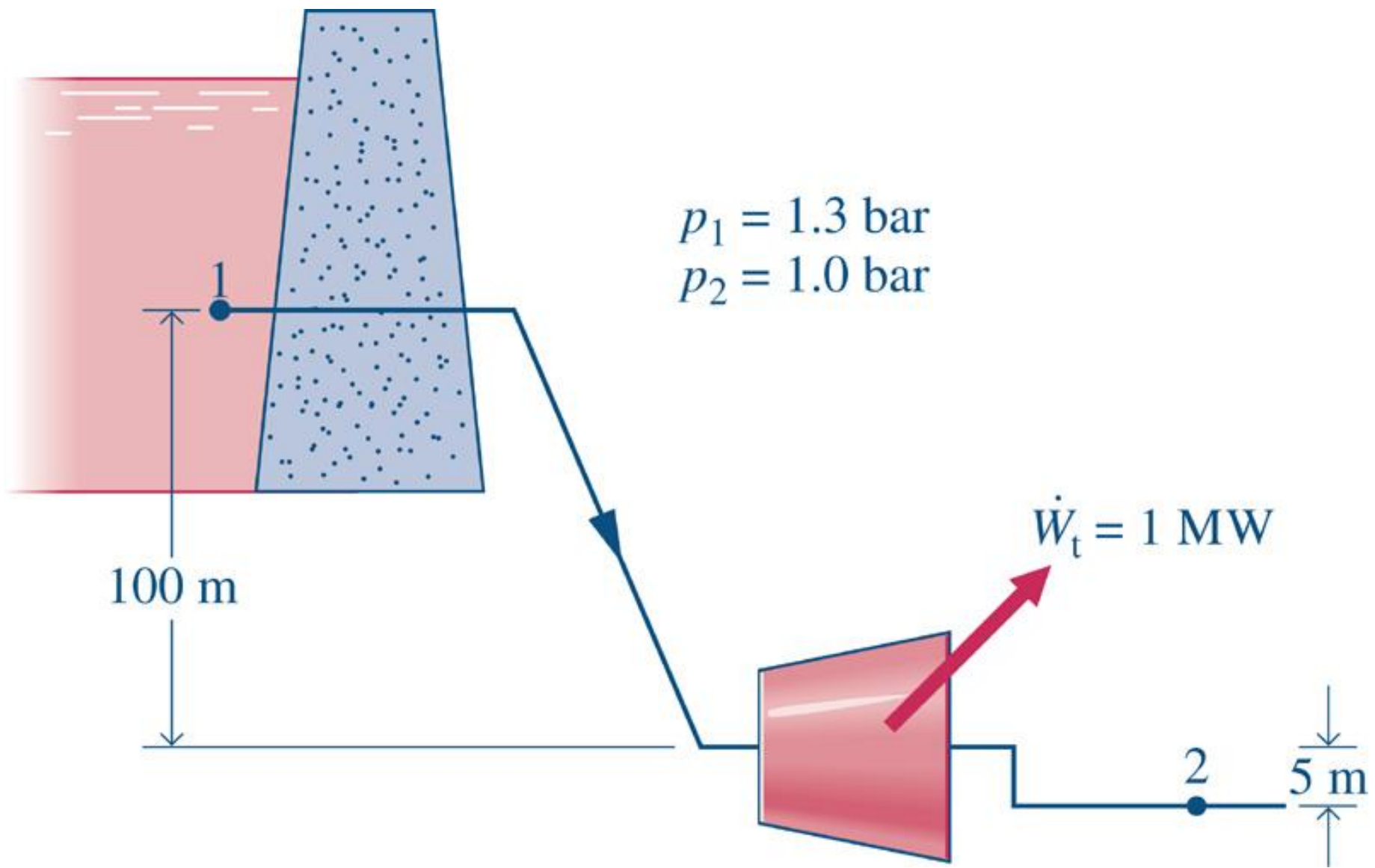


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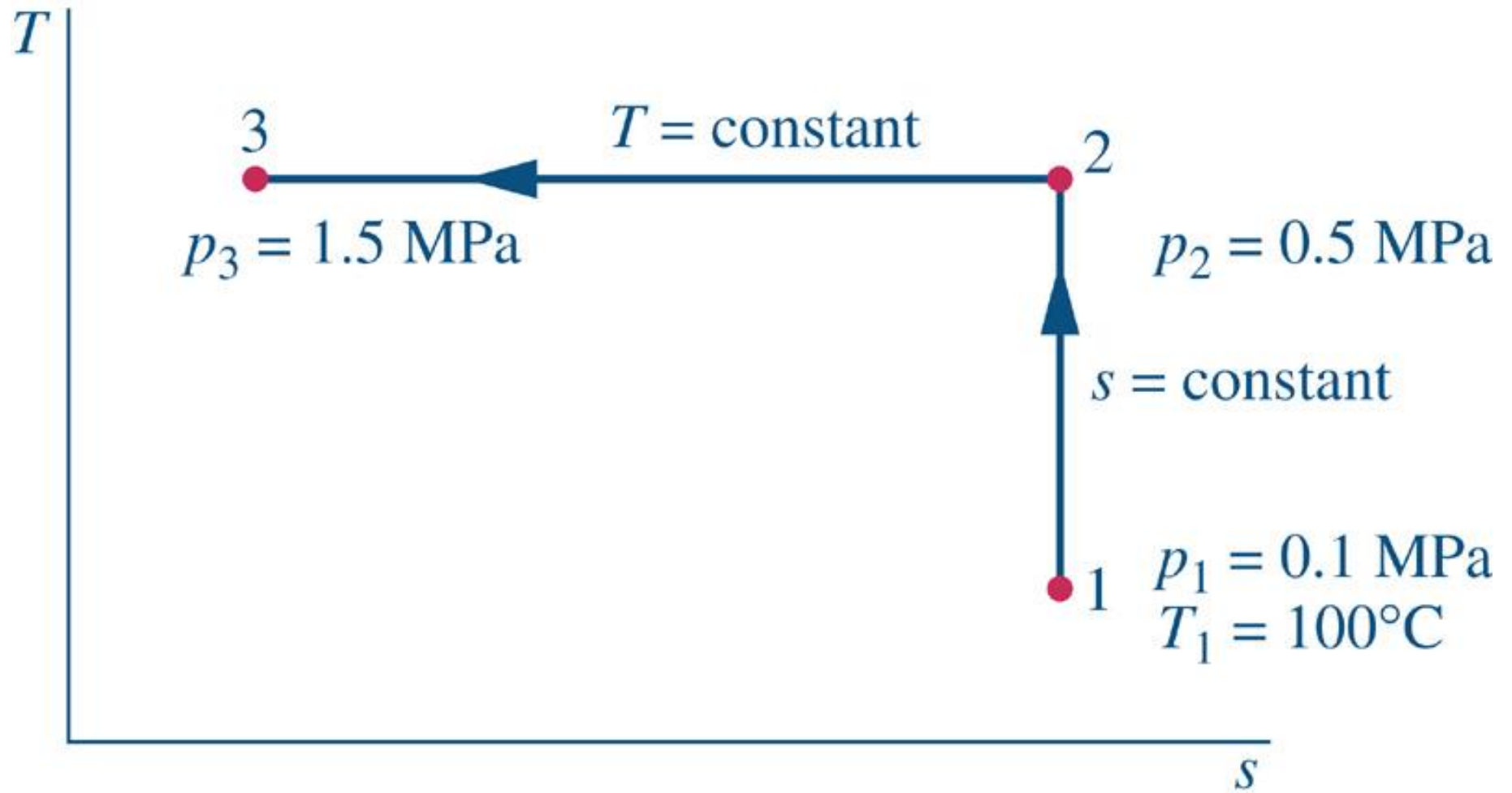


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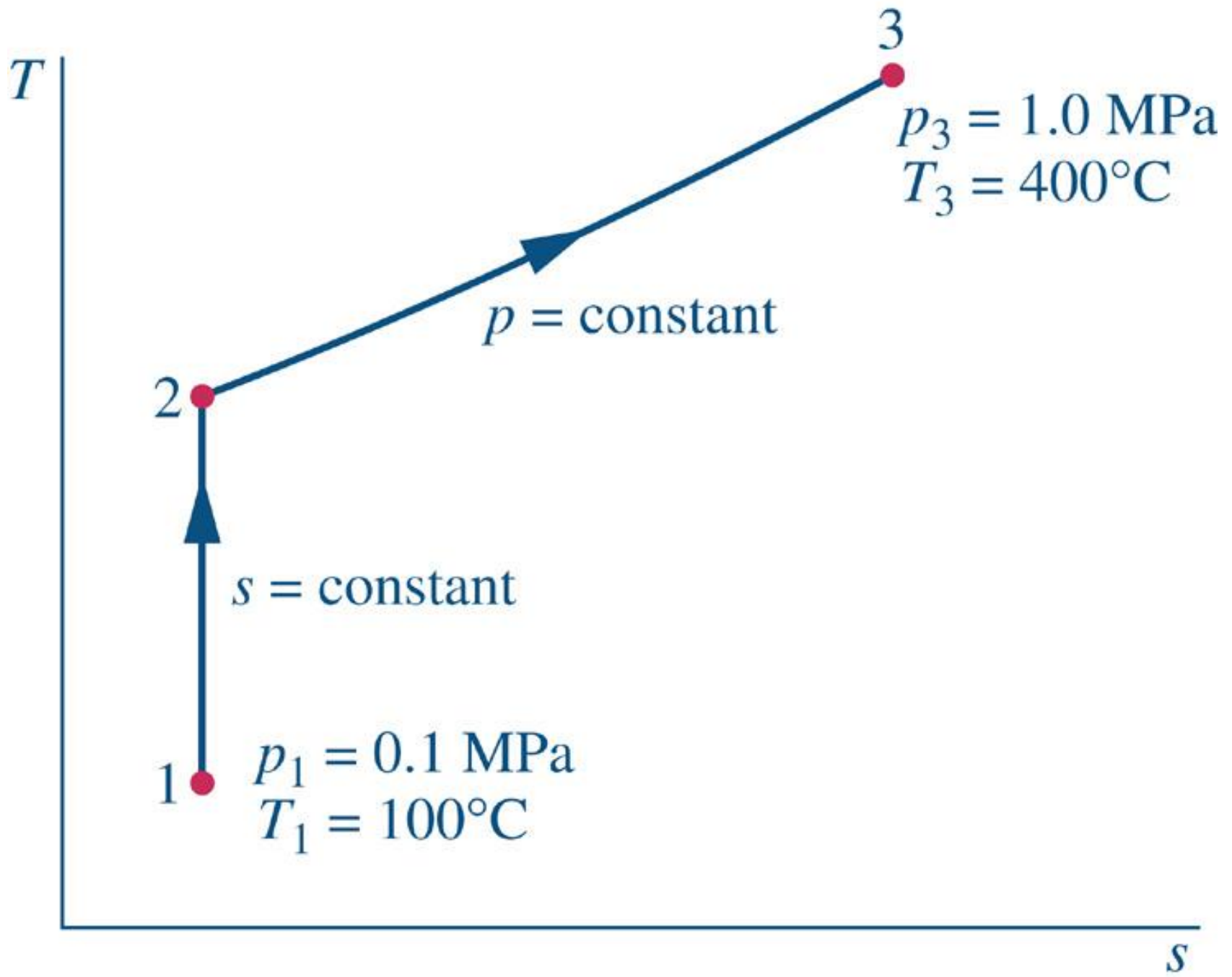


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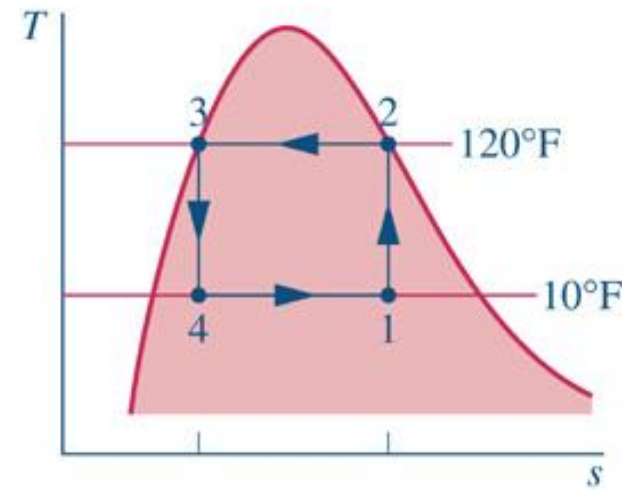
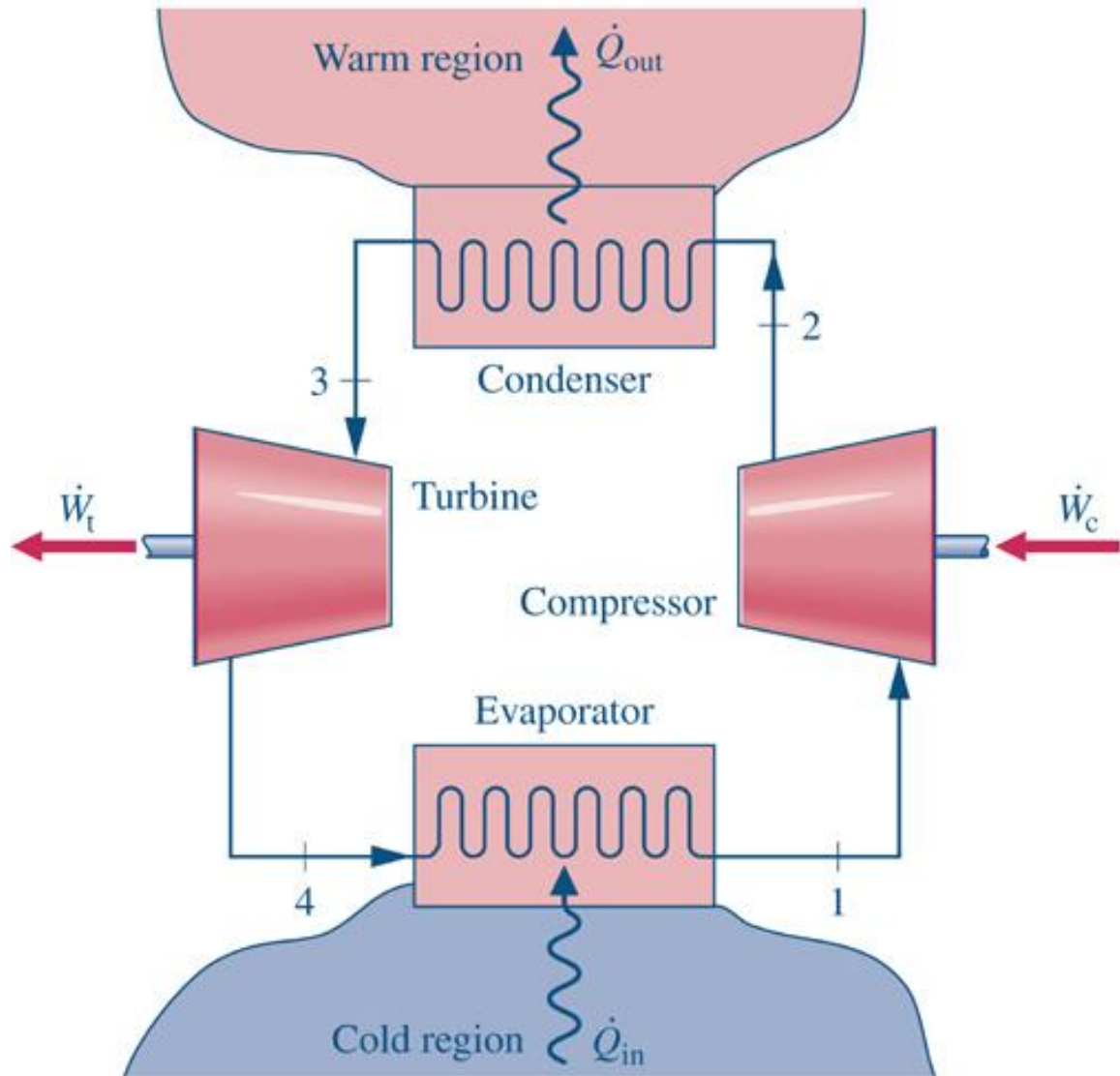


Fig06_P6

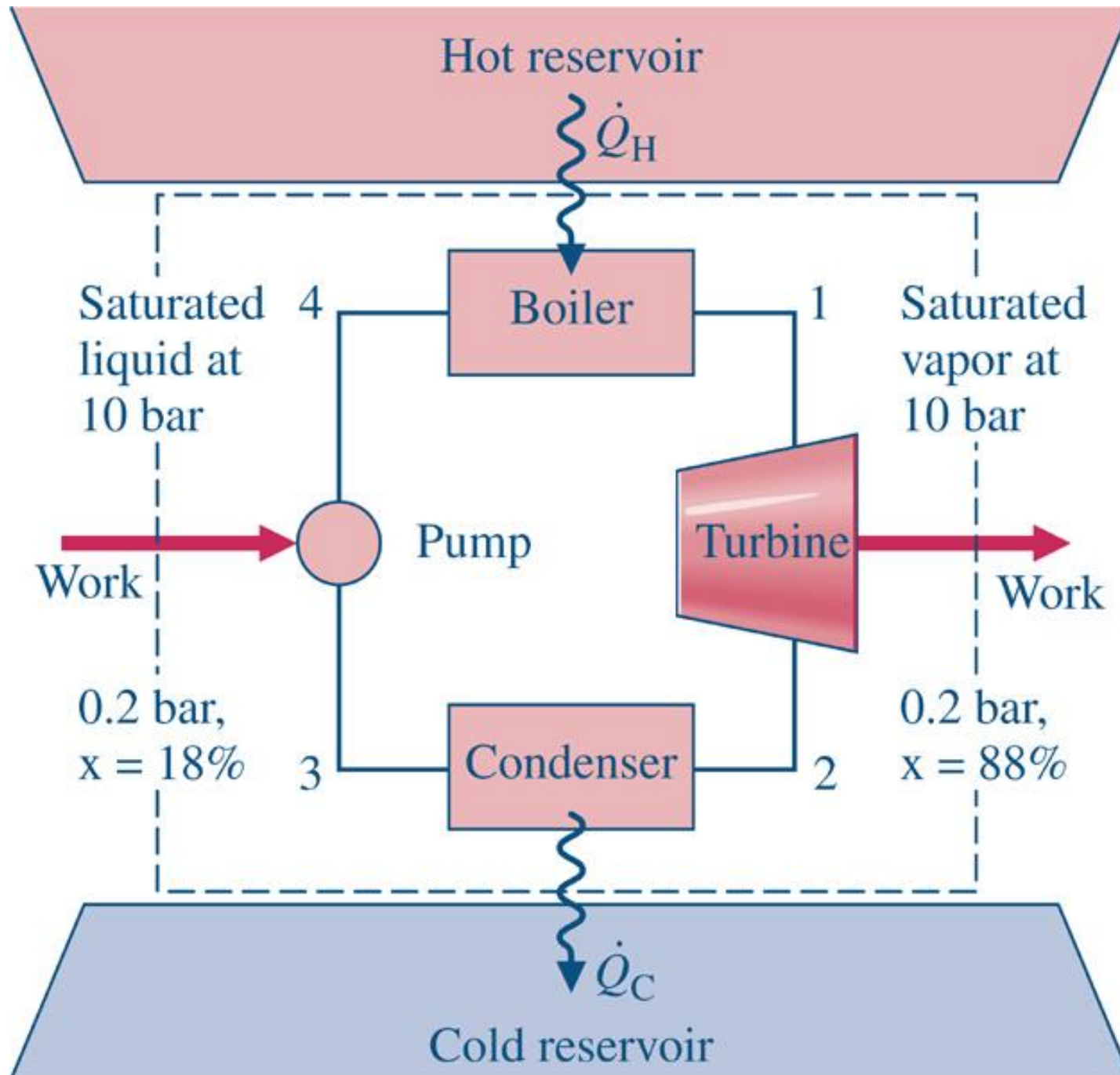


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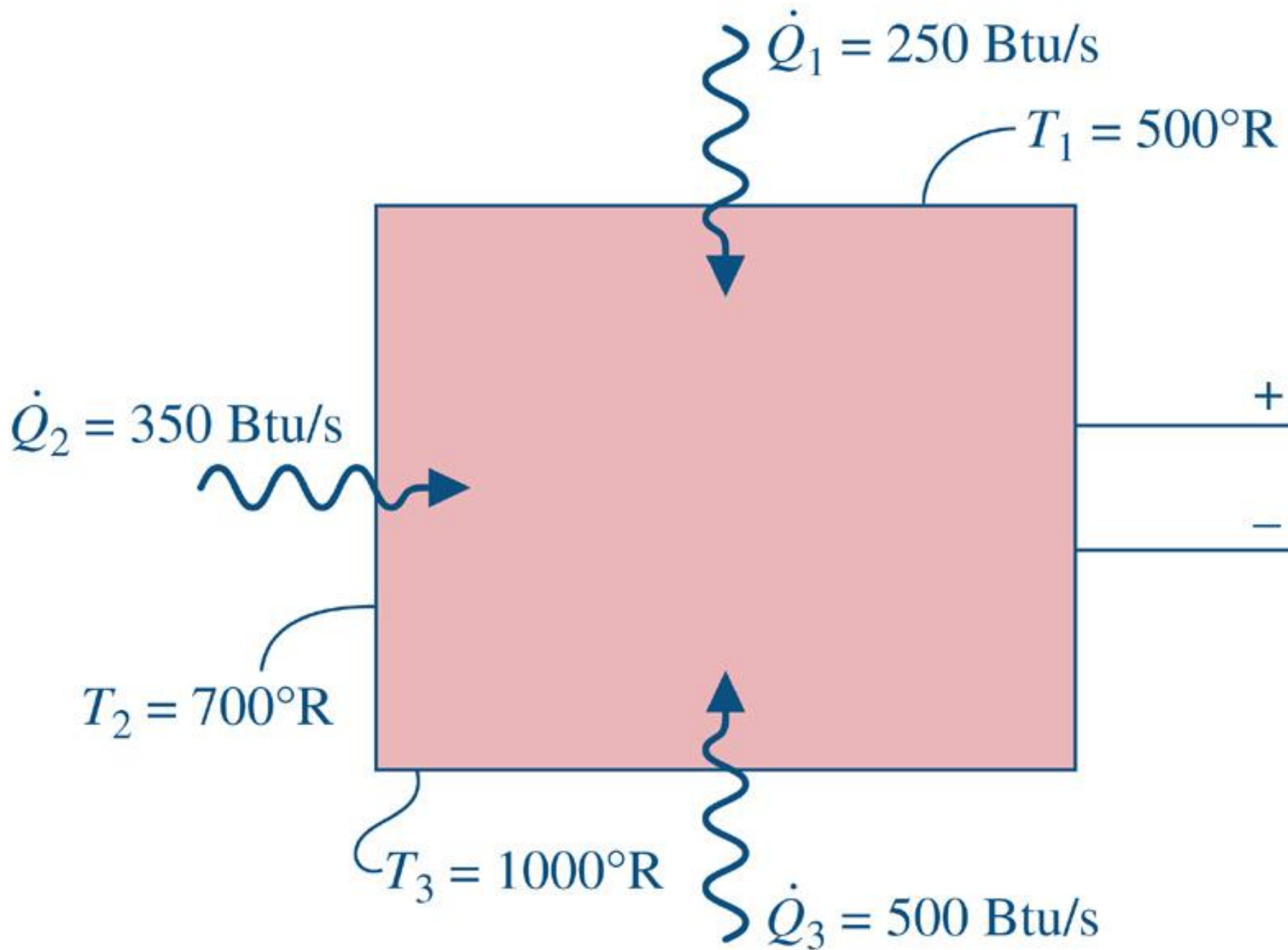


Fig06_P6



Fig06_P6

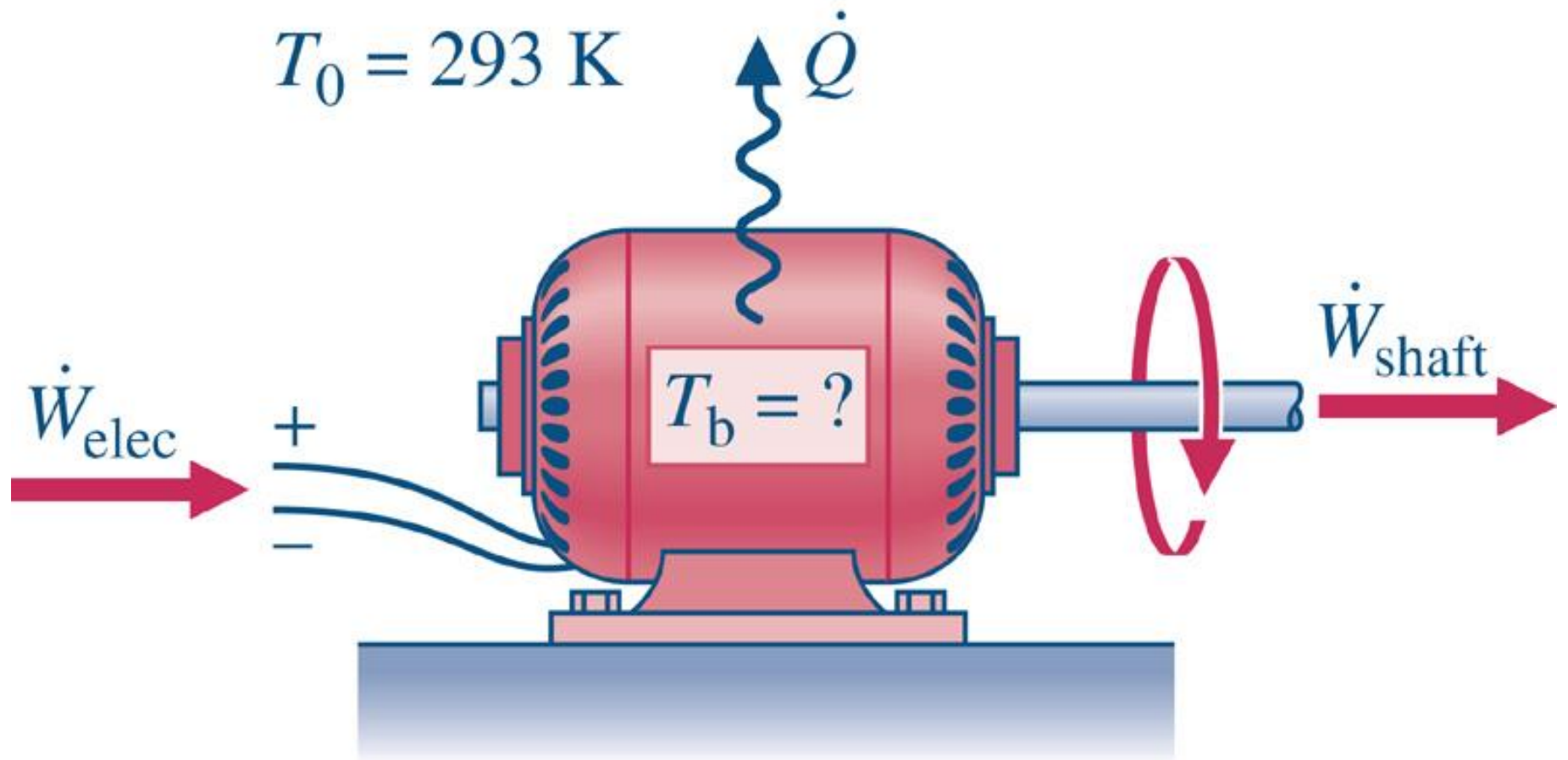


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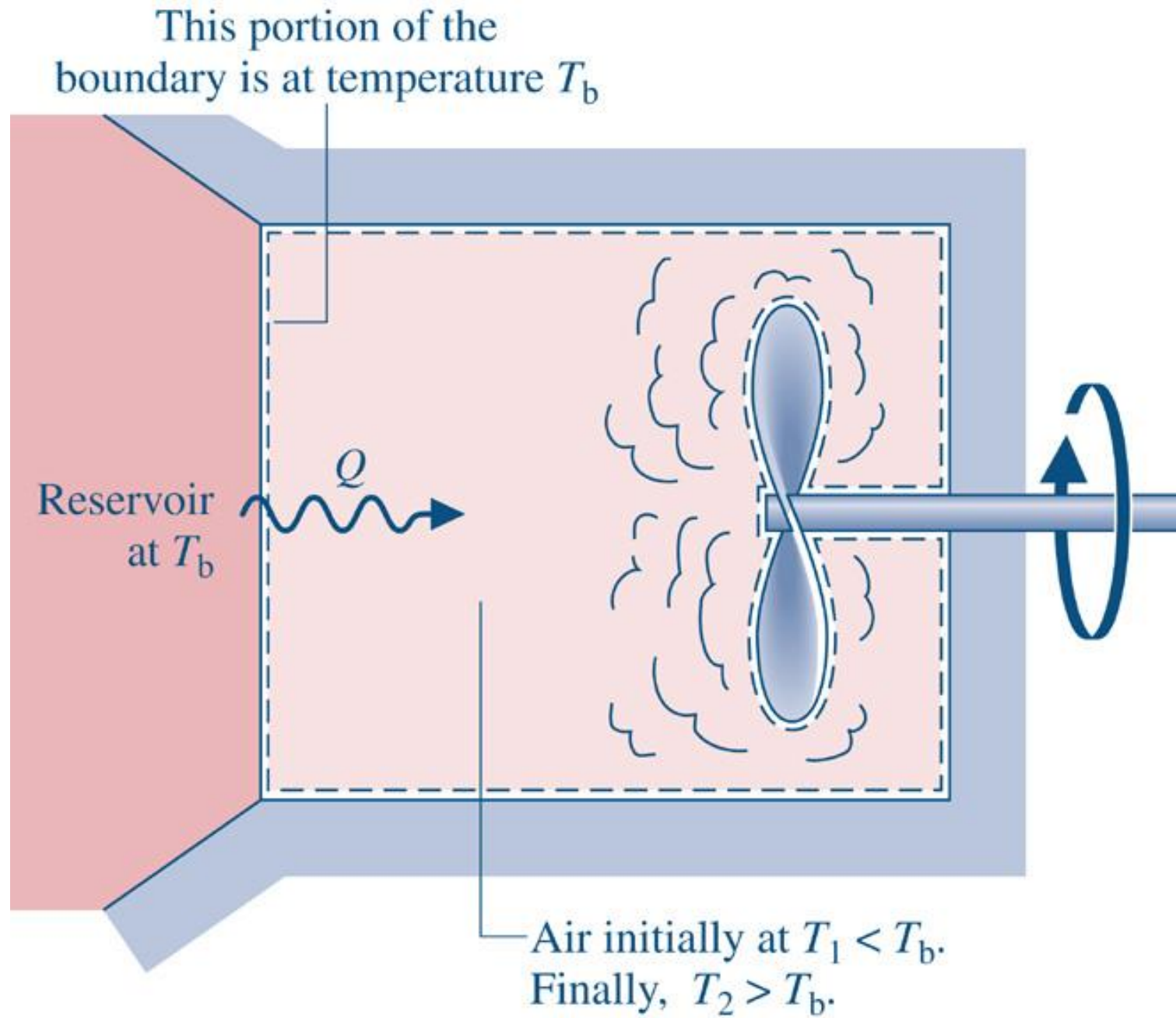


Fig06_P6

Initially: steam
at 3.0 MPa, 280°C

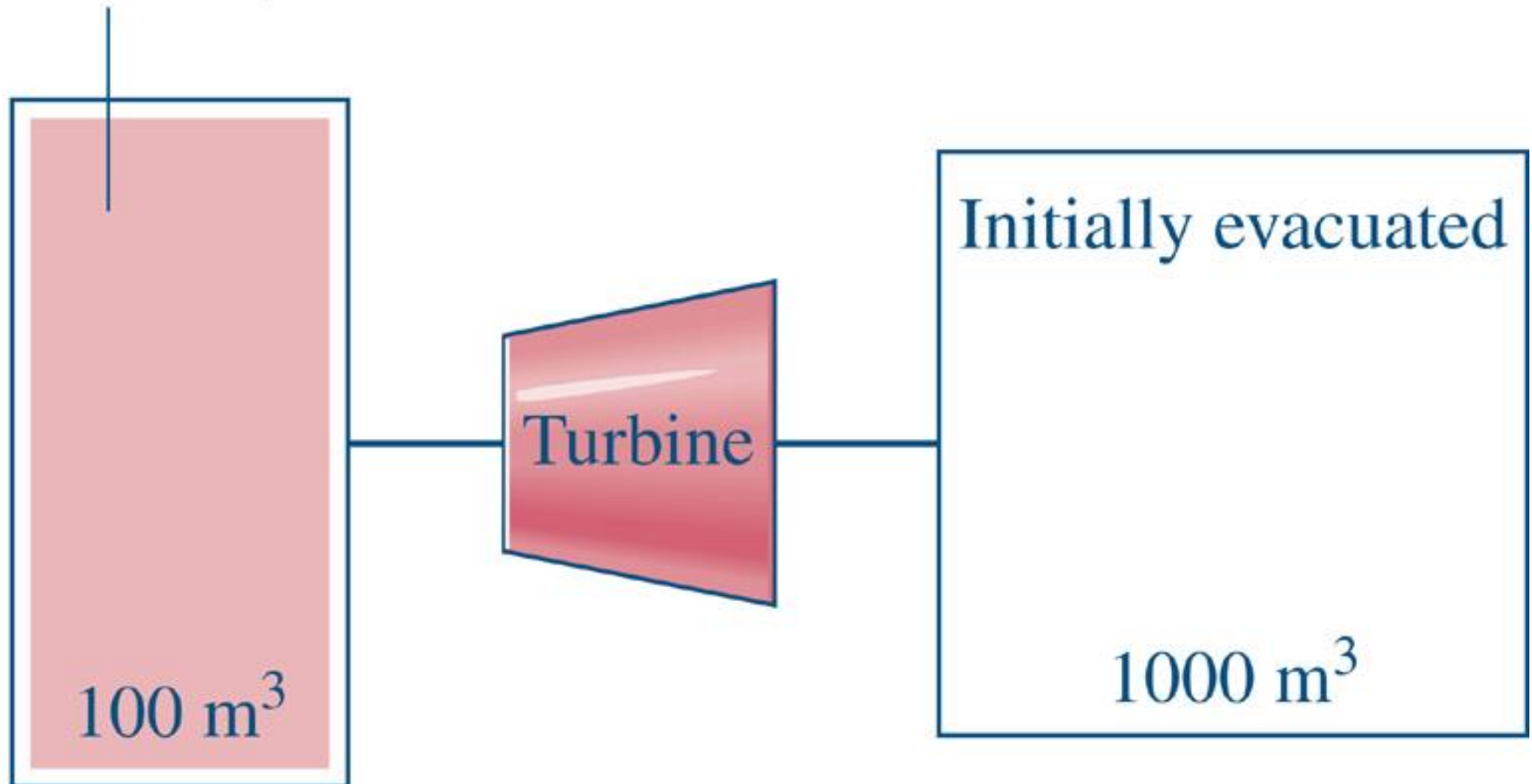


Fig06_P6

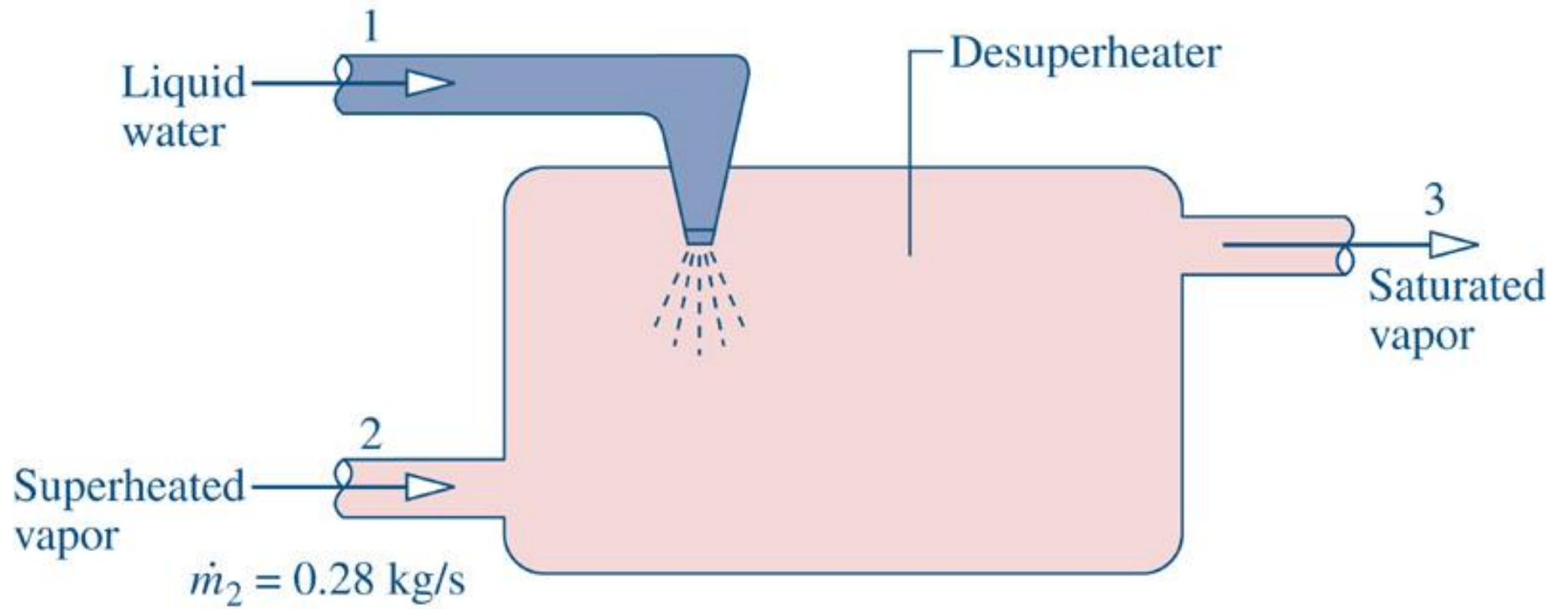


Fig06_P6

Power out = 1174.9 kW

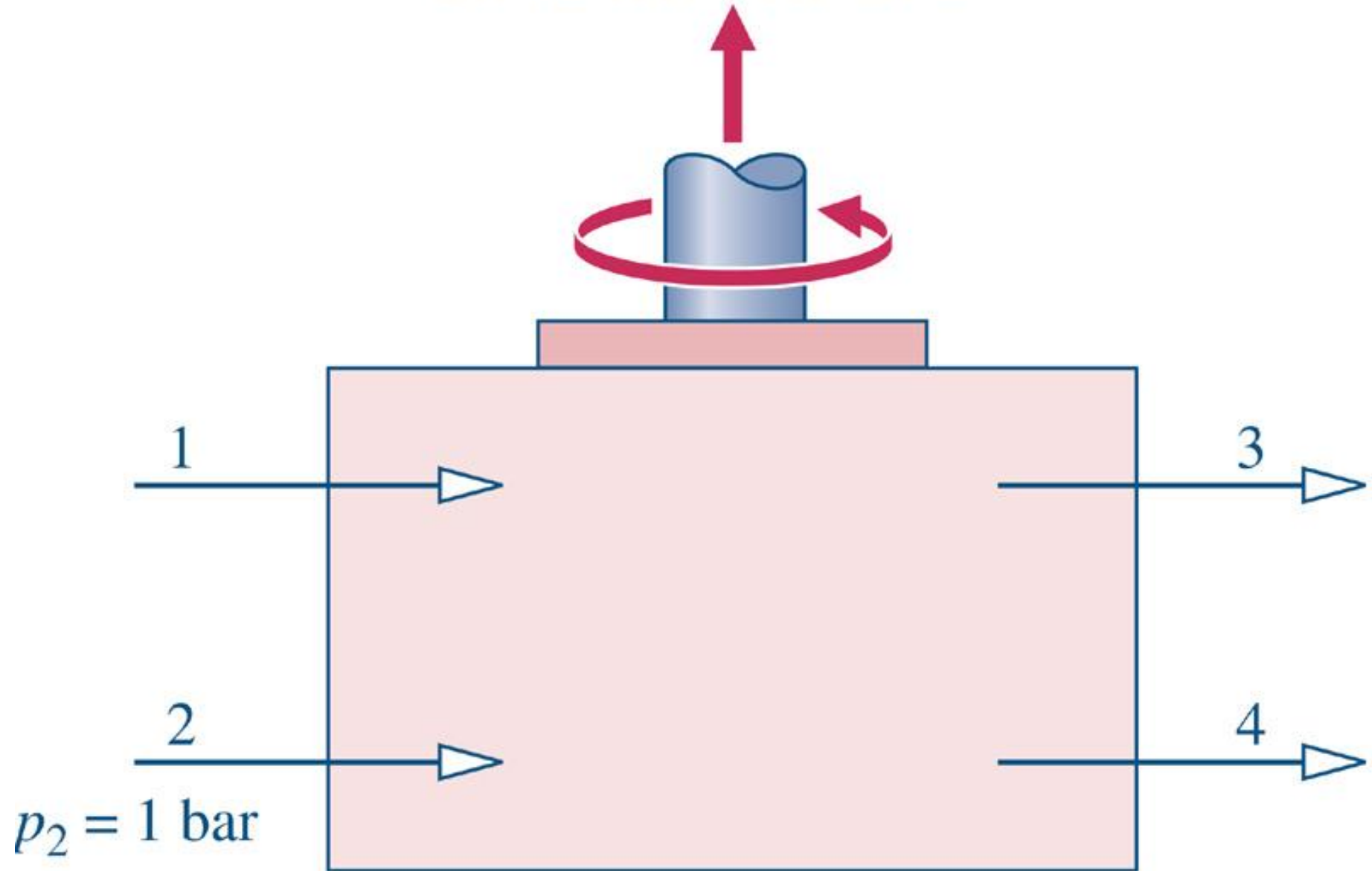


Fig06_P6

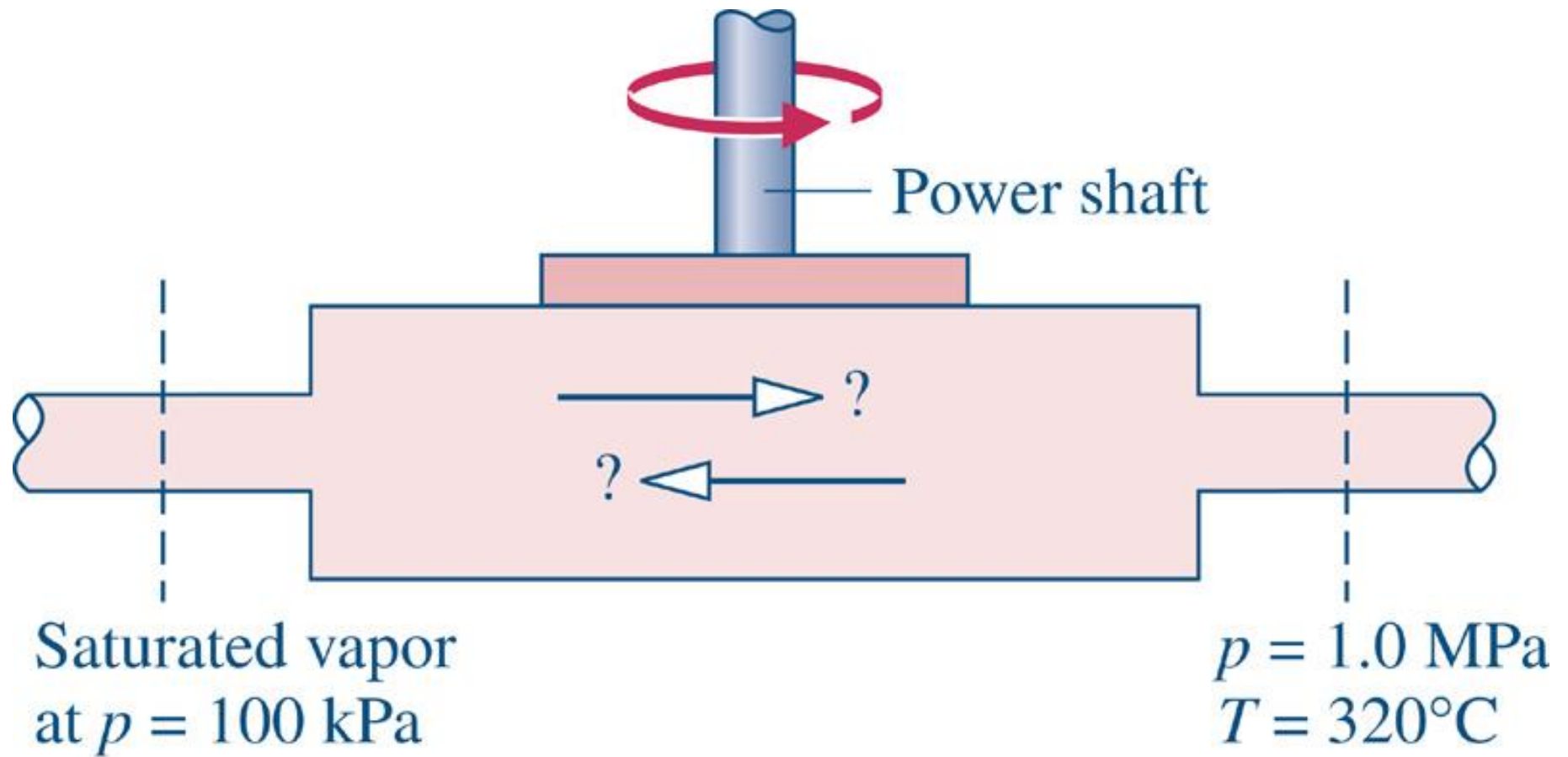


Fig06_P6

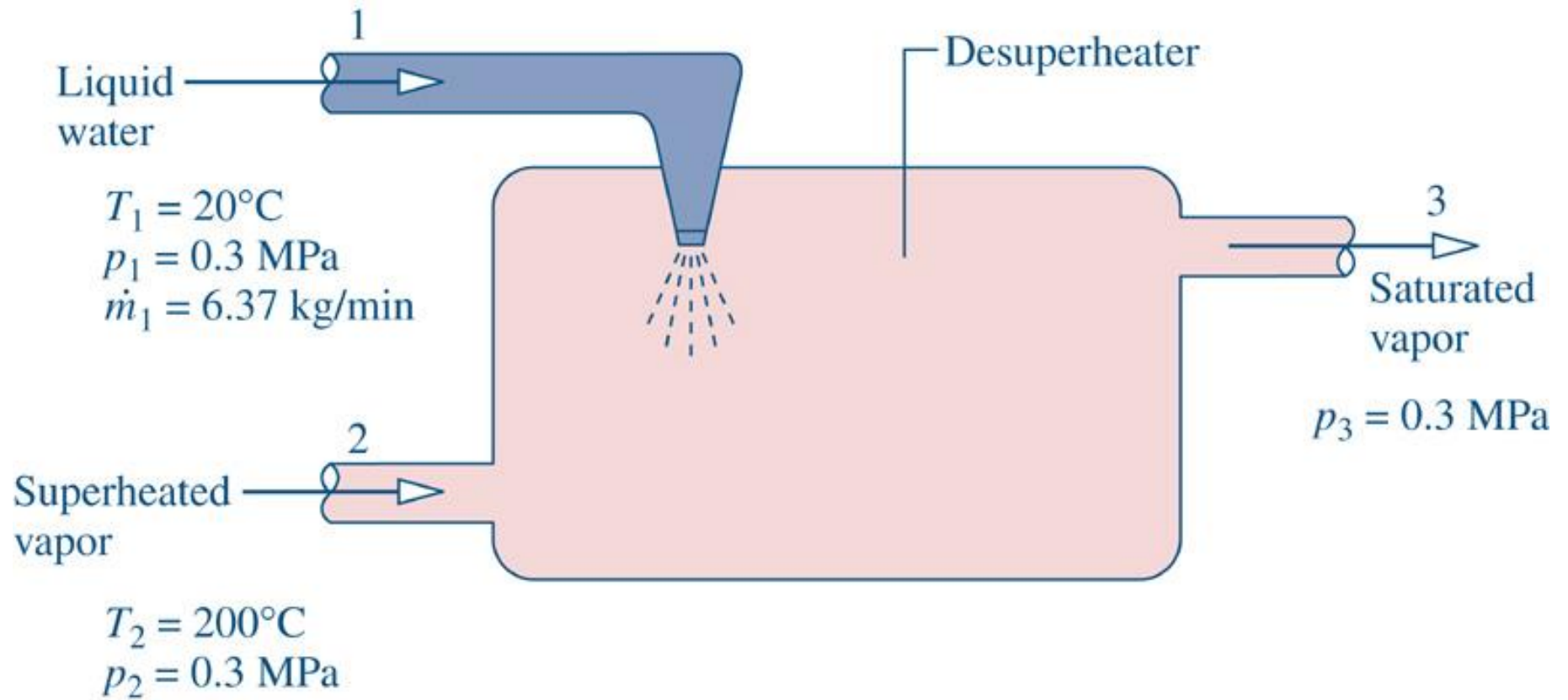


Fig06_P6

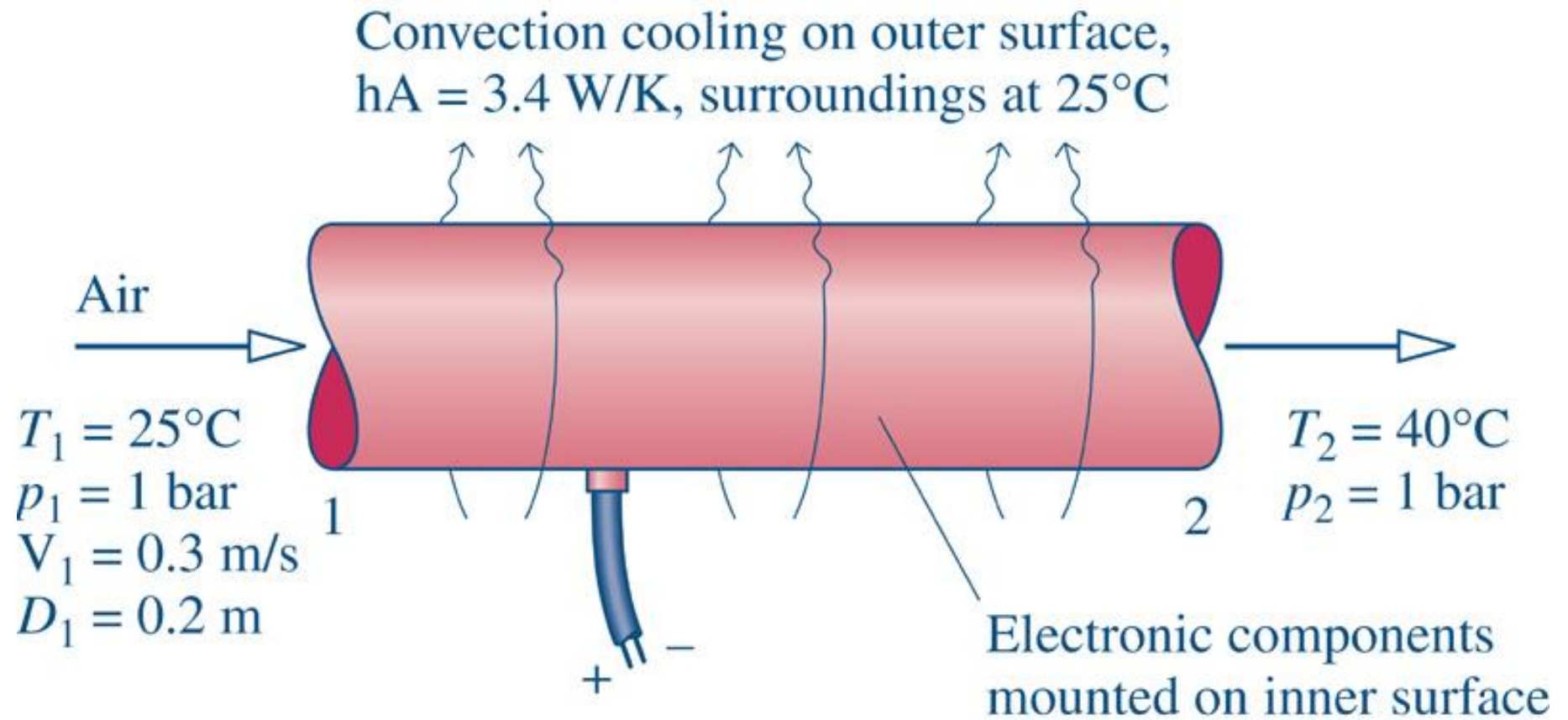


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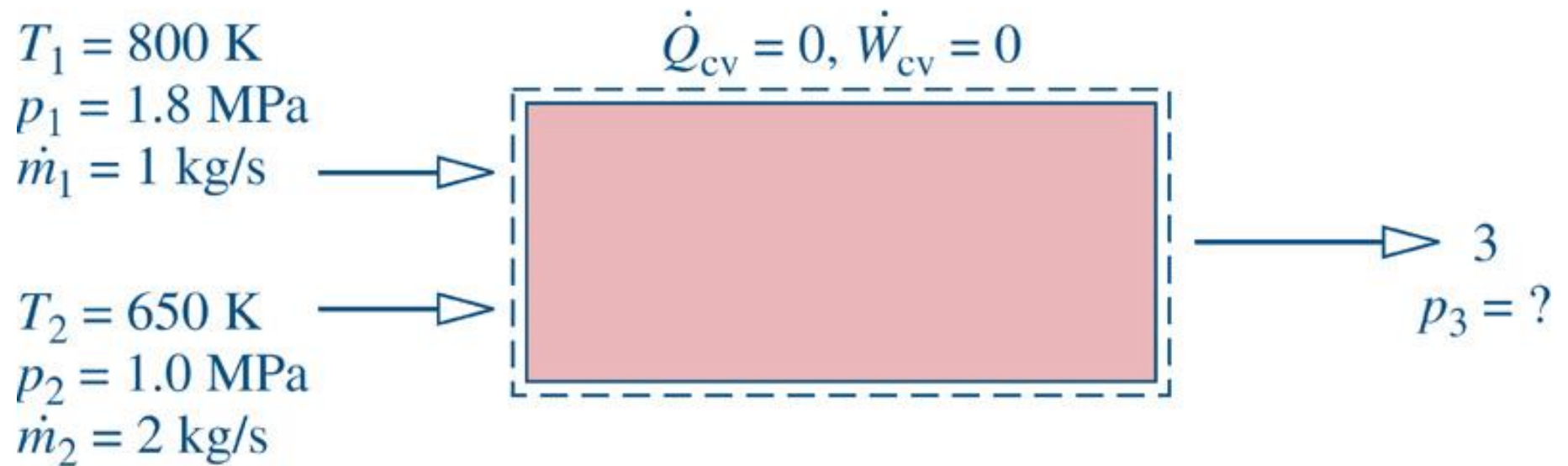


Fig06_P6

Ideal Gas Model Review

Equations of State:

$$pv = RT \quad (3.32)$$

$$pV = mRT \quad (3.33)$$

Changes in u and h :

$$u(T_2) - u(T_1) = \int_{T_1}^{T_2} c_v(T) dT \quad (3.40)$$

$$h(T_2) - h(T_1) = \int_{T_1}^{T_2} c_p(T) dT \quad (3.43)$$

| Constant Specific Heats | Variable Specific Heats |
|---|--|
| $u(T_2) - u(T_1) = c_v(T_2 - T_1) \quad (3.50)$ | $u(T)$ and $h(T)$ are evaluated from Tables A-22 for air (mass basis) and Tables A-23 for several other gases (molar basis). |
| $h(T_2) - h(T_1) = c_p(T_2 - T_1) \quad (3.51)$ | |
| See Tables A-20, 21 for c_v and c_p data. | |

The integral of Eq. 6.18 can be expressed in terms of s° as follows

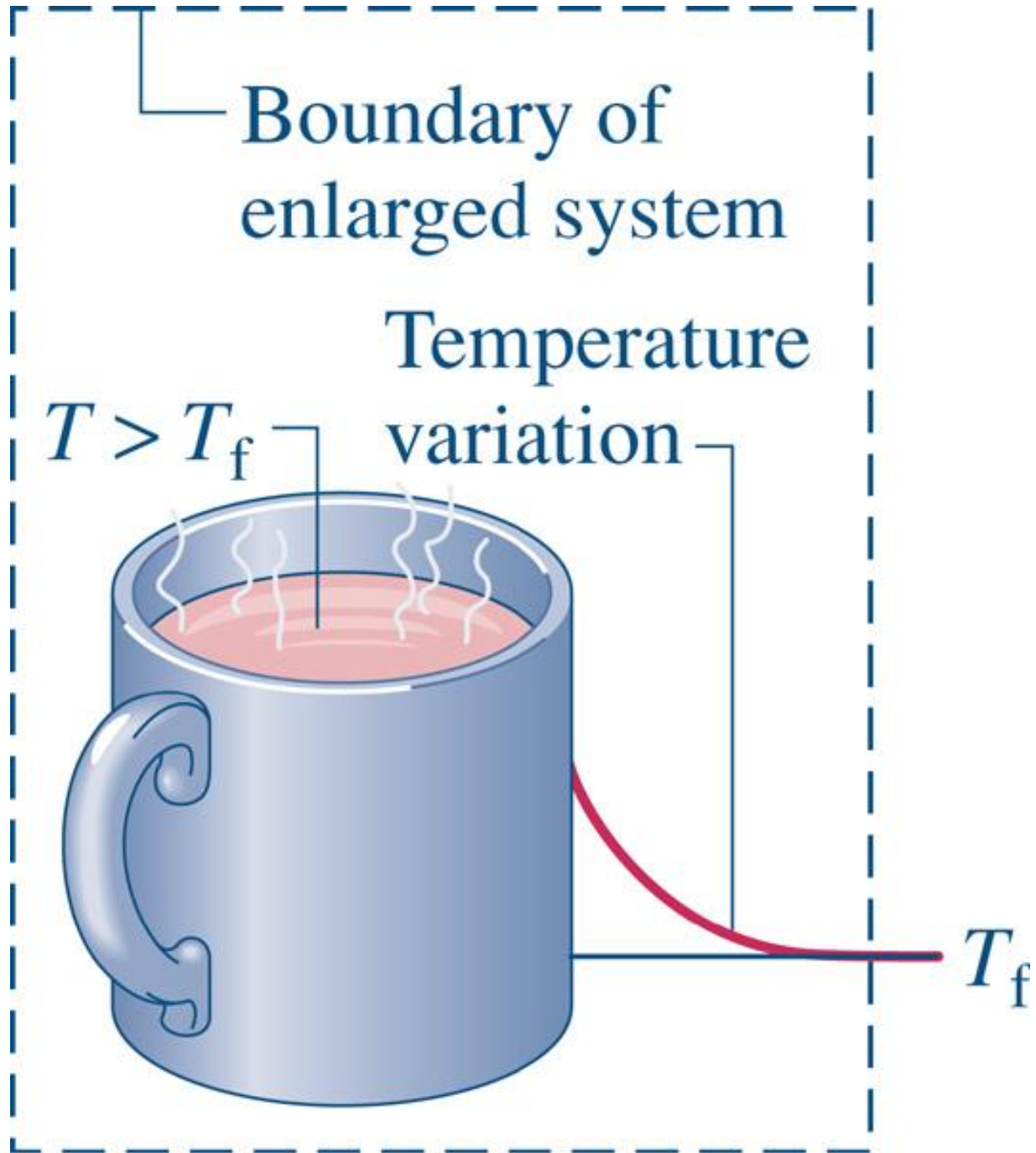
$$\begin{aligned} \int_{T_1}^{T_2} c_p \frac{dT}{T} &= \int_{T'}^{T_2} c_p \frac{dT}{T} - \int_{T'}^{T_1} c_p \frac{dT}{T} \\ &= s^\circ(T_2) - s^\circ(T_1) \end{aligned}$$

Thus, Eq. 6.18 can be written as

$$s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R \ln \frac{p_2}{p_1} \quad (6.20a)$$

or on a per mole basis as

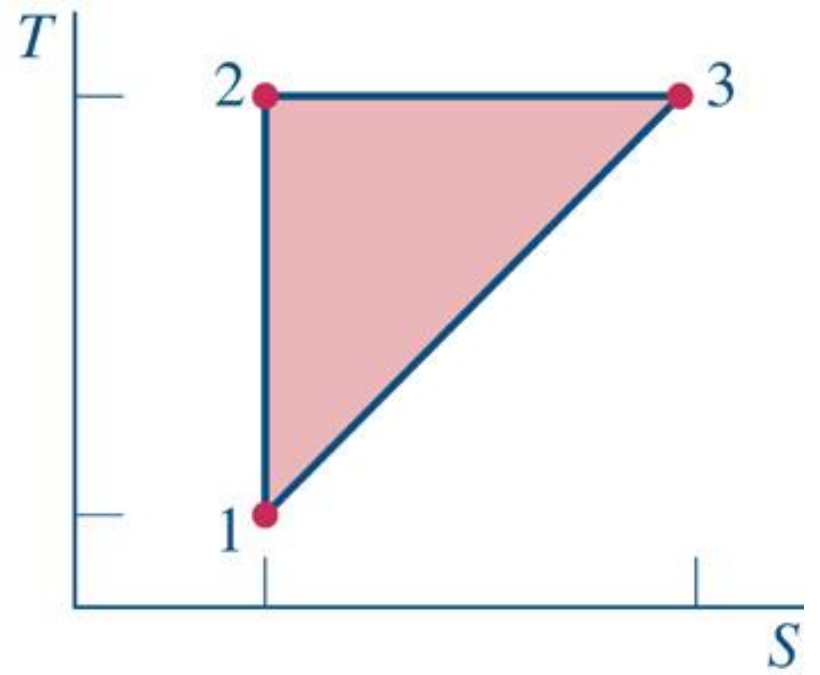
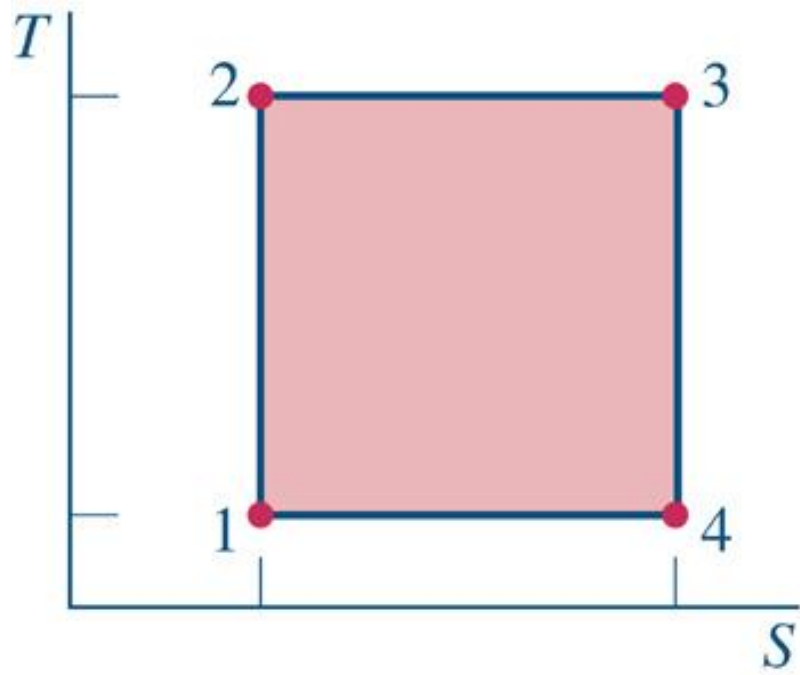
$$\bar{s}(T_2, p_2) - \bar{s}(T_1, p_1) = \bar{s}^\circ(T_2) - \bar{s}^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1} \quad (6.20b)$$





UmFig06_02_pg280





UnFig06_04_pg311