Problem 1.8-3. Work and heat

(A→B)

$$W = -P_A(V_B - V_A) = -4 \cdot 10^3 [J]$$

$$\Delta U = 2.5\left(P_B V_B - P_A V_A\right) = 10^4 [J] \qquad Q = \Delta U - W = 1.4 \cdot 10^4 [J]$$

(B→C)

$$W = -\int_B^B P(V)dV = 7 \cdot 10^3 [J]$$

$$\Delta U = 2.5\left(P_C V_C - P_B V_B\right) = -2.5 \cdot 10^3 [J] \qquad Q = \Delta U - W = -9.5 \cdot 10^3 [J]$$

(C→A) $W = 0$ $\qquad Q = \Delta U = 2.5\left(P_A V_A - P_C V_C\right) = -7.5 \cdot 10^3 [J]$

(A→B, parabola)

$$W = -\int_B^B P(V)dV = -2.67 \cdot 10^3 [J]$$

$$Q = \Delta U - W = 12.67 \cdot 10^3 [J]$$

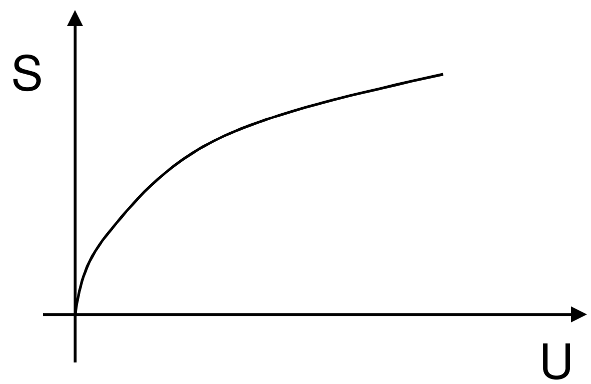
Consistent: a, c, e, g, i

Inconsistent: b, d, f, h, j

Problem 1.10-1. Shapes of S vs U

Most difficult: b, c, f and i

b) $$S = \left(\frac{R}{\theta^2}\right)^{1/3}\left(\frac{NU}{V}\right)^{2/3}$$

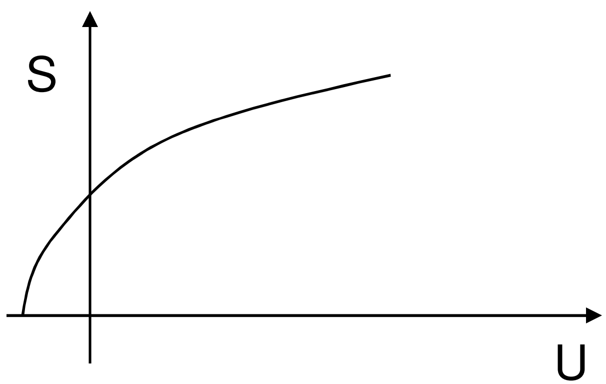


Inconsistent with the postulates because entropy does not scale linearly with the size of the system

$$\lambda S = \left(\frac{R}{\theta^2}\right)^{1/3}\left(\frac{\lambda N \lambda U}{\lambda V}\right)^{2/3} \Rightarrow \lambda = \lambda^{2/3}$$

not true for arbitrary λ

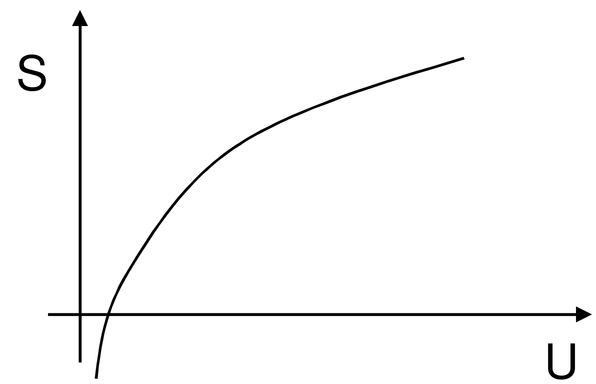
c) $$S = \left(\frac{R}{\theta}\right)^{1/2}\left(NU + \frac{R\theta V^2}{v_0^2}\right)^{1/2}$$



Consistent with the postulates, zero of energy is arbitrary.

Problem 1.10-1. Shapes of S vs U

f) $$S = NR\ln\left(\frac{UV}{N^2 R\theta v_0}\right)$$

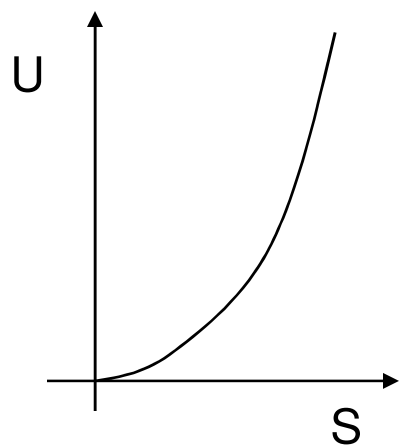


Inconsistent with postulate IV,
S should be zero at $\partial S/\partial U \rightarrow \infty$

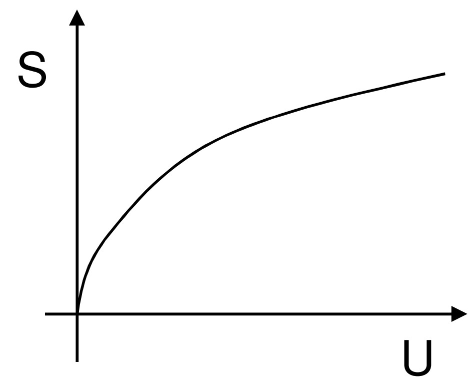
i) $$U = \frac{v_0\theta}{R}\frac{S^2}{V}\exp\left(\frac{S}{NR}\right)$$

Consistent with the postulates

First plot
U vs S

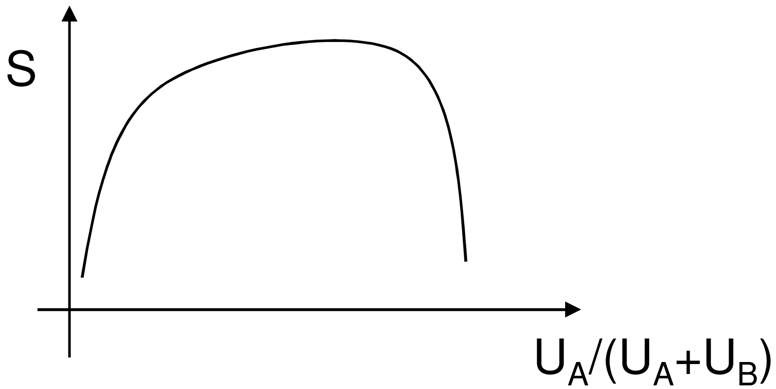


Then rotate it
around the U/S
bisector to
obtain S vs U



Problem 1.10-3. Entropy maximum for a composite system

For a *composite* system ($S=S_1+S_2$)



$$\left(NV\right)_A = 27\cdot 10^{-6}$$

$$\left(NV\right)_A = 8\cdot 10^{-6}$$

$$U = U_A + U_B = 80$$

$$\frac{S}{const} = 3U_A^{1/3} + 2\left(U - U_A\right)^{1/3}$$ - need to maximize with respect to U_A

$$0 = \frac{\partial}{\partial U_A}\left[3U_A^{1/3} + 2\left(U - U_A\right)^{1/3}\right] \Rightarrow 0 = U_A^{-2/3} - \frac{2}{3}\left(U - U_A\right)^{-2/3}$$

Solving for U_A

$$U_A = \frac{U}{1+\left(2/3\right)^{3/2}} = 51.8[J]$$

Problem 2.3-4. Restrictions due to the Postulates

$$S = AU^n V^m N^r$$

Most common problem: forgetting to check if entropy is additive (extensive)

When we increase the size of a thermodynamic system by a factor of λ, all extensive variables should scale with λ: U→ λU, V→ λV, N→ λN, S→ λS.

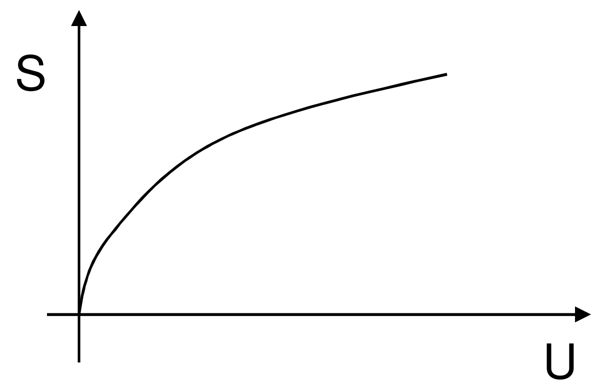
Subjecting the fundamental relation to this scaling transformation:

$$\lambda S = A(\lambda U)^n (\lambda V)^m (\lambda N)^r = \lambda^{n+m+r} AU^n V^m N^r \quad \Longrightarrow$$

$$\Longrightarrow \quad \lambda = \lambda^{n+m+r} \qquad \boxed{n+m+r=1}$$

Problem 2.3-4. Restrictions due to the Postulates

$$S = AU^n V^m N^r$$



S must be increasing with U, so n>0

$$\frac{\partial S}{\partial U} \to \infty$$ as S→0, therefore n<1 $\Rightarrow$ $\boxed{0<n<1}$

Additional condition: P should increase with U/V:

$$\frac{P}{T} = \frac{\partial S}{\partial V} = mAU^n V^{m-1} N^r \qquad \frac{1}{T} = \frac{\partial S}{\partial U} = nAU^{n-1} V^m N^r$$

$$\Rightarrow \quad P = T\frac{\partial S}{\partial V} = \frac{m}{n}\frac{U}{V} \quad \Rightarrow \quad \frac{m}{n} > 0 \quad \Rightarrow \quad \boxed{m > 0}$$

Problem 2.6-3. Energy in Equilibrium

$$U^{(1)} + U^{(2)} = 2.5\times10^3[J] \qquad N^{(1)} = 2 \qquad N^{(2)} = 3 \qquad \boxed{U^{(1)} = ?}$$

The equations of state of the two systems are:

$$\frac{1}{T^{(1)}} = \frac{3}{2}R\frac{N^{(1)}}{U^{(1)}} \qquad \frac{1}{T^{(2)}} = \frac{5}{2}R\frac{N^{(2)}}{U^{(2)}}$$

Since the two systems are in thermal equilibrium:

$$T^{(1)} = T^{(2)} \Rightarrow \frac{3}{2}\frac{N^{(1)}}{U^{(1)}} = \frac{5}{2}\frac{N^{(2)}}{U^{(2)}} \Rightarrow U^{(2)} = \frac{15}{6}U^{(1)}$$

$$U^{(1)} + U^{(2)} = 2.5\times10^3[J] \Rightarrow U^{(1)} + \frac{15}{6}U^{(1)} = 2.5\times10^3[J] \Rightarrow \boxed{U^{(1)} = 714[J]}$$

Problem 2.7-3. The Indeterminate Problem of Thermodynamics

a) Show that $P^{(1)} = P^{(2)}$

Since the piston is adiabatic, $\delta Q^{(1,2)} = 0$ and thus $dU^{(1,2)} = -P^{(1,2)} dV^{(1,2)}$

Since the composite system is isolated $dU \equiv dU^{(1)} + dU^{(2)} = 0$

$$\Rightarrow \quad -P^{(1)} dV^{(1)} - P^{(2)} dV^{(2)} = 0$$

Since the total volume of the composite system is constant $dV^{(1)} = -dV^{(2)}$

Therefore, $P^{(1)} = P^{(2)}$ follows.

b) Show that thermodynamics does not tell us what the temperatures of the two systems are

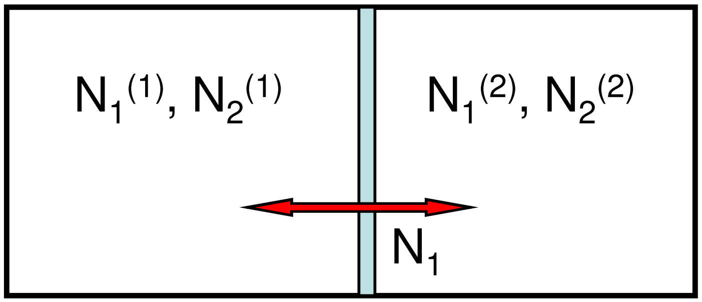
The entropy maximum condition requires:

$$dS \equiv dS^{(1)} + dS^{(2)} = \frac{dU^{(1)}}{T^{(1)}} + \frac{P^{(1)}}{T^{(1)}} dV^{(1)} + \frac{dU^{(2)}}{T^{(2)}} + \frac{P^{(2)}}{T^{(2)}} dV^{(2)} = 0 \quad \Rightarrow$$

$$\frac{dU^{(1)} + P^{(1)} dV^{(1)}}{T^{(1)}} + \frac{dU^{(2)} + P^{(2)} dV^{(2)}}{T^{(2)}} = 0$$

The numerators in this expression vanish identically because of the adiabaticity of the wall, therefore the denominators ($T^{(1)}$ and $T^{(2)}$) can be arbitrary and still satisfy the entropy maximum condition.

Problem 2.8-1. Semi-permeable partition



Two different gases N_1 and N_2

N_1 can freely flow through the membrane while N_2 cannot.

Important: $P^{(1)} \neq P^{(2)}$ although one of the gas components can freely penetrate the membrane

P is intensive parameter conjugate to volume, volume is constrained

Equilibrium conditions:

$$\frac{\mu_1^{(1)}}{T^{(1)}} = \frac{\mu_1^{(2)}}{T^{(2)}}$$

$$T^{(1)} = T^{(2)}$$

Conservation conditions:

$$N_1^{(1)} + N_1^{(2)} = \left(N_1^{(1)} + N_1^{(2)}\right)_{initial}$$

$$U^{(1)} + U^{(2)} = \left(U^{(1)} + U^{(2)}\right)_{initial}$$

Problem 2.8-1. Semi-permeable partition

$$S = NA + NR\ln\left(\frac{U^{3/2}V}{N^{5/2}}\right) - N_1 R\ln\left(\frac{N_1}{N}\right) - N_2 R\ln\left(\frac{N_2}{N}\right) \qquad N = N_1 + N_2$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3NR}{2U} \Rightarrow U = \frac{3NRT}{2}$$

Solve for T

$$\begin{cases} T^{(1)} = T^{(2)} = T \\ U^{(1)} + U^{(2)} = \left(U^{(1)} + U^{(2)}\right)_{initial} \end{cases}$$

$$T = 272.73[K]$$

$$\frac{\mu_1}{T} = \frac{\partial S}{\partial N_1} = \ldots$$

Here, when differentiating do not forget that $N=N_1+N_2$

After some algebra:

$$\frac{\mu_1}{T} = A - \frac{5}{2}R + R\ln\left(\frac{U^{3/2}V}{N_1\left(N_1+N_2\right)^{3/2}}\right)$$

Problem 2.8-1. Semi-permeable partition

Solve for N_1

$$\begin{cases} N_1^{(1)} + N_1^{(2)} = \left(N_1^{(1)} + N_1^{(2)}\right)_{initial} \\ \dfrac{\mu_1^{(1)}}{T} = \dfrac{\mu_1^{(2)}}{T} \end{cases} \Rightarrow N_1^{(1)} = N_1^{(2)} = 0.75$$

To find P:

$$\frac{\partial S}{\partial V} = \frac{P}{T} = \frac{NR}{V} \qquad P^{(1)} = \frac{\left(N_1^{(1)} + N_2^{(1)}\right)RT}{V^{(1)}}$$

$$P^{(1)} = 680[kPa]$$

Similarly: $P^{(2)} = 567[kPa]$

Numerical Problem

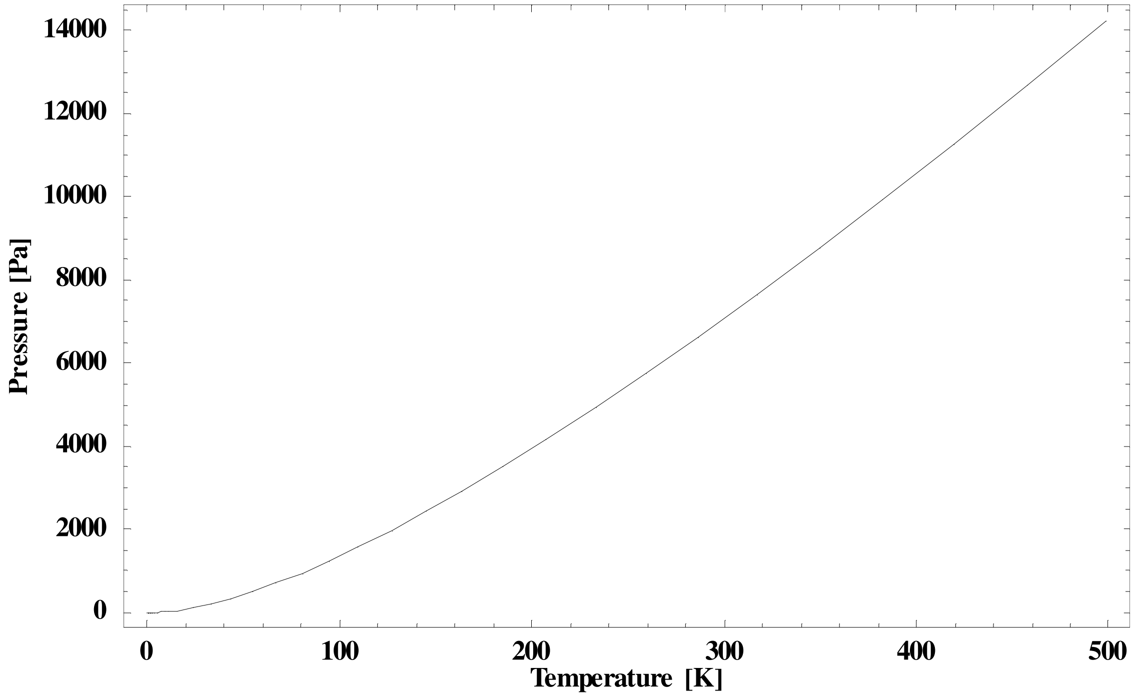
First calculate P and T by differentiating the fundamental relation. Then use the parametric plot of P(S) and T(S) to plot the P(T) dependence.

```
Nu = 1; V = 0.01; U0 = 1;
```

$$T[S\_] := U0 \frac{S}{V}\left(2 + \frac{S}{Nu}\right) Exp\left[\frac{S}{Nu}\right];$$

$$P[S\_] := U0 \frac{S^2}{V^2} Exp\left[\frac{S}{Nu}\right];$$

```
ParametricPlot[{T[S], P[S]}, {S, 0, 0.8}, Frame -> True, TextStyle -> {FontFamily -> "Times", FontWeight -> "Bold", FontSize -> 14},
  FrameLabel -> {Temperature " "[K], Pressure " "[Pa]}, PlotRange -> All]
```



- Graphics -