

3_2 Thermodynamics and Geothermal Systems

Recap:

Heat supplied to the crust (~70km deep) by convection - but conduction dominates in the crust
 Hydrothermal regimes concentrated in - destructive, constructive and hot-spot areas
 EGS low-grade power ubiquitous

Recovery of thermal energy - requires a heat-transfer mechanism
 Generating power requires an energy conversion mechanism - flash to steam

Movies:

Allam Cycle: <https://www.youtube.com/watch?v=vFcbv1TkoU>

Resources: WG3

Thermodynamics: https://en.wikipedia.org/wiki/Laws_of_thermodynamics

Motivation:

1. Motivation [10%] Provide context for the topic. *Use of relevant public domain videos* are a useful method for this. Why is this particular topic or sub-topic important in the broad view of geothermal energy engineering?

1. Generation of electricity requires conversion of energy - heat to work to electricity
2. Dissolution and precipitation of minerals (scaling) is controlled by thermodynamics
3. Water in geothermal reservoirs exists in vapor and liquid and may transit between states

Scientific Questions:

2. Scientific Questions to be Answered/Outline [10%] What questions arise from the motivation. What are the sub-topical areas that address these scientific questions.

Background on Laws of Thermodynamics:

1. First Law:

a. Conservation of Energy

Energy can neither be created or be destroyed - it is conserved
All forms of energy are equivalent

b. Internal Energy

FIRST LAW OF THERMODYNAMICS - ENERGY EQUATION

First law of thermodynamics:

Rate of increase of total stored energy in the system = Net rate of addition by heat transfer + Net rate of addition by work transfer

$$\frac{d}{dt} \int_{CV} \rho e \, dV = (\dot{Q}_{net})_{cv} + (\dot{W}_{net})_{cv}$$

where e is total stored energy (per unit mass), $e = \tilde{u} + \frac{V^2}{2} + gZ$

\tilde{u} = Internal energy per unit mass
 $\frac{V^2}{2}$ = Kinetic energy per unit mass
 gZ = Potential energy per unit mass

NB: \dot{Q} and \dot{W} defined (+ve) going into system (-ve) leaving system
 i.e. Opposite to (V.R.) concept

SIMPLIFICATIONS TO THE GENERAL SYSTEM

$$\dot{Q}_{net} + \dot{W}_{net} = \frac{d}{dt} \int_{CV} \rho (e + \frac{V^2}{2} + gZ) \, dV$$

Steady system: $\frac{d}{dt} \rightarrow 0$
 Adiabatic: $\dot{Q}_{net} = 0$
 Stagnant system: $V = 0 \therefore V \cdot \vec{R} = 0$
 No transfer of power: $\dot{W}_{net} = 0$

For '1-D' system: (Steady)

$$\dot{m} [(e_{out} - e_{in}) + \frac{1}{2}(V_{out}^2 - V_{in}^2) + g(Z_{out} - Z_{in})] = \dot{Q}_{net} + \dot{W}_{net}$$

or Denoting enthalpy as $h = \tilde{u} + \frac{p}{\rho}$ $e = \tilde{u} + \frac{V^2}{2} + gZ$

$$\dot{m} [h_{out} - h_{in} + \frac{V_{out}^2 - V_{in}^2}{2} + g(Z_{out} - Z_{in})] = \dot{Q}_{net} + \dot{W}_{net}$$

\tilde{u} = Internal energy per unit mass.
 e = Total energy

COMPARISON WITH BERNOULLI EXPRESSION

Use '1-D' equation: but set $\dot{W} = 0$ (no abstraction from system).

$$\dot{m} [\tilde{u}_{out} - \tilde{u}_{in} + \frac{p_{out} - p_{in}}{\rho} + \frac{V_{out}^2 - V_{in}^2}{2} + g(Z_{out} - Z_{in})] = \dot{Q}_{net}$$

Divide by mass flow rate, \dot{m} , as

$$\frac{p_{out}}{\rho} + \frac{V_{out}^2}{2} + gZ_{out} = \frac{p_{in}}{\rho} + \frac{V_{in}^2}{2} + gZ_{in} - (\tilde{u}_{out} - \tilde{u}_{in} - \frac{q_{net}}{\dot{m}})$$

$q_{net} = \frac{\dot{Q}_{net}}{\dot{m}}$

Energy loss due to "real" effects.

- Friction (viscous flow)
- Compressibility of flow

$$\Delta E = E_f - E_i$$

which states that the change in internal energy (ΔE) is equal to the internal energy of the system in its final state (E_f) minus the initial internal energy (E_i).

This simple equation is profoundly important. It establishes the significance of knowing the internal energy at the end points of a process that affects a system. It is the difference between these end points that determines how much energy is required to heat a space, generate power, or cool a room. It also emphasizes that the pathway that was followed to get from the initial to the final states has absolutely no significance for the change in internal energy. For example, imagine a volume of gas contained in a cylinder and that the cylinder is a perfect insulator—that is, it will not allow heat to be added to or removed from the gas it contains. Imagine, too, that one end of the cylinder is movable (Figure 3.1). There are an infinite number of ways to get from some specified initial state (the cylinder on the left of the figure) to the final state (the cylinder on the right of the figure), two of which are depicted in the figure. In the sequence A1 → A2, the gas undergoes simple compression in a single step. In this case, the pressure (P) and temperature (T) of the gas in the initial state are increased to P_2 and T_2 , respectively, and the internal energy change (ΔE) is equal to $E_2 - E_1$. In the sequence B1 → B2 → B3 → B4 → B5, the gas undergoes a series of changes in pressure and temperature before reaching the same P_2 and T_2 in the A1 to A2 sequence. Each step results in a change in the internal energy:

$$\Delta E = E_{B5} + E_{B4} + E_{B3} + E_{B2} - E_{B1}$$

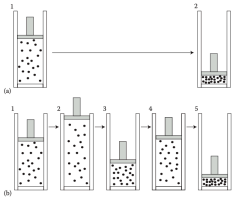


FIGURE 3.1 Diagrammatic representation of a cylinder of gas that follows two pathways (a and b) from one set of pressure and temperature conditions to another. Path (a) represents a single-stage compression, whereas path (b) involves two expansion and two compression stages. For both pathways, the change in the internal energy (ΔE) is the same. The black dots in the cylinder schematically represent the gas molecules. In reality, there are an infinite number of pathways that could be followed that would achieve the same result.

If we were to measure the internal energy at the end of each step in B, we would find that

$$E_{B1} + E_{B2} + E_{B3} + E_{B4} = E_2$$

which results in

$$\Delta E = E_2 + E_1 + E_2 + E_2 + E_2 - E_1 - E_1$$

Thus, regardless of the complexity of the path that is followed in getting from one set of conditions to another, or to put it another way, regardless of how much work one does to a system in moving it from one state to another, the internal energy will always be the difference between the initial and final states.

PRESSURE-VOLUME WORK

The conclusion that is inescapable is that any change in the internal energy of a system is solely the result of the work *done to* the system, or that the system performs, and any heat *added to* or taken from the system:

$$\Delta E = q + w \quad (3.1)$$

Mechanical work is performed when a force applied to a point, surface, or volume results in displacement of that point, surface, or volume. As an example, consider the changes in the cylinder in Figure 3.1. As the piston moves from its position in B1 to its position in B2, if there is an external force applied to the piston, mechanical work is performed by the gas as its volume increases and forces the piston to move. Hence, the element of mechanical work is defined by

$$dW = -P \times dV \quad (3.2)$$

By convention, mechanical work done on a system is positive, whereas work done by a system is negative. Work performed is, therefore, equivalent to the change in volume between the two states:

$$w = -P \times (V_2 - V_1) = -P \times \Delta V \quad (3.3)$$

ENTHALPY

It follows from this discussion that in a process in which no change in volume occurs, no mechanical work is performed and any change in internal energy is solely related to heat added to or removed from the system:

$$\Delta E = q_p \quad (3.4)$$

The subscript v is used to indicate heat at constant volume; similarly, a subscript p would refer to a constant pressure condition. If, however, a change in volume occurs at constant pressure and heat is also added to or removed from the system, the change in internal energy is

$$\Delta E = q_p - (P \times \Delta V) \quad (3.5)$$

The heat added to or removed from the system at constant pressure is called the enthalpy (H) and the change in enthalpy (ΔH) that is realized when moving from one state to another is defined as

$$\Delta H = H_2 - H_1 = [E_2 + (P \times V_2)] - [E_1 + (P \times V_1)] + q_p \quad (3.6)$$

Enthalpy is an important system property in geothermal power applications because it provides a means for establishing the behavior of a system in the subsurface and allows for evaluation of the useful energy that can be extracted from a working fluid. It has units of J/kg. We will consider this topic in more detail in Chapter 10.

c. Pressure-Volume Work (above)

d. Enthalpy (above)

$$\text{Enthalpy } \check{h} = \check{u} + P/\rho$$

$$\text{and: } \rho \rho [(\check{h}_{out} - \check{h}_{in}) + \frac{1}{2} (V_{out}^2 - V_{in}^2) + g(z_{out} - z_{in})] = \dot{Q}_{net,in} + \dot{W}_{net,in}$$

2. Second Law:

Entropy always increases

a. Efficiency

$$\text{Efficiency} = -W/Q$$

b. Carnot Cycle

$$PV = nRT$$

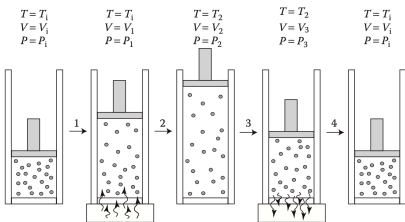


FIGURE 3.2 Diagrammatic representation of a gas cylinder following the steps in a Carnot cycle. Subscripts 1 and 4 represent, respectively, initial and final conditions. The arrows at the base of the cylinders in steps 1 and 3 indicate the direction of heat flow, relative to the heat reservoirs that are indicated by the boxes at the bases of the cylinders.

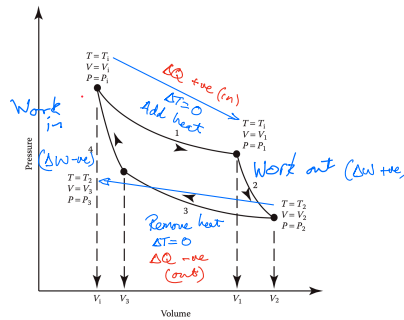


FIGURE 3.3 Pressure versus volume graph for the series of changes for the Carnot cycle depicted in Figure 3.2.

c. Heat Capacity

In general: $C = dq_p / dT \quad \sim \quad C dT = dq_p$

Also: $\Delta H = \Delta(E + P \times V) = q_p$

At constant pressure ($\Delta P = 0$): $\Delta H = q_p \rightarrow dH = C_p dT$

At constant volume ($\Delta V = 0$): $\Delta E = q_v \rightarrow dE = C_v dT$

and $dW = C_v dT$

d. Entropy

By definition:

$$dS = dq_r / T$$

A measure of unattainable heat.

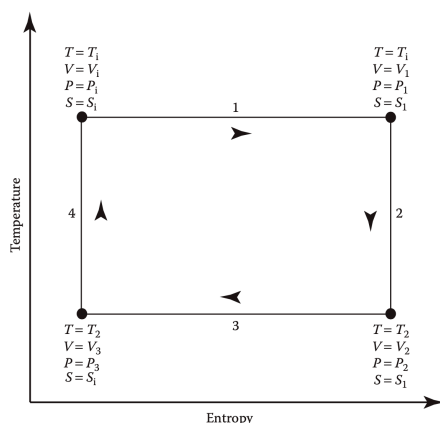


FIGURE 3.4 Temperature versus entropy graph for the same pathways indicated in the pressure versus volume graph in Figure 3.3.

3. Gibbs Function and Gibbs Energy (dG):

Defines the energy available within a system at a reference state \rightarrow and therefore the ability of that system to do work, relative to another state

$$\Delta H = \Delta (E + P \times V) = q_r$$

Then $\Delta H - q_r = 0$ for example \rightarrow $\begin{cases} dq_r = T dS \\ dq_r = C dT \end{cases}$
(In a closed invariant system)

$$\Delta G_{P,T} = \Delta H_{P_1, T_1} - T \times \Delta S_{P_1, T_1} + \int_{T_1}^T \Delta C_p dT - T \times \int_{T_1}^T (\Delta C_p / T) dT + \int_{P_1}^T \Delta V dP \quad (3.15)$$

where:

$\Delta G_{P,T}$ is the Gibbs energy at P and T

$\Delta H_{P_1, T_1}$ is the enthalpy at some standard state, which is usually selected to be 1 bar (0.1 MPa) pressure and 25°C (298 K)

$\Delta S_{P_1, T_1}$ is the entropy at the standard state

ΔC_p is the constant pressure heat capacity

ΔV is the change in volume

ΔG gives the change in energy within the system.

$$G_{P,T} - G_{STP} = (H_{P,T} - H_{STP}) - T \times (S_{P,T} - S_{STP})$$

$$\Delta \text{Gibbs Energy} = \Delta \text{Enthalpy} - T \times \Delta \text{Entropy}$$

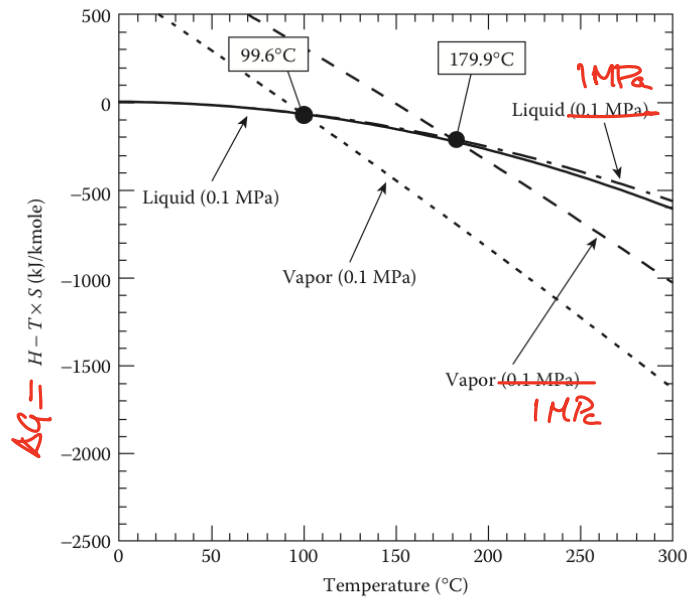


FIGURE 3.5 The isobaric changes in Gibbs energy at 0.1 MPa and 1.0 MPa as a function of temperature, for liquid and vapor H₂O. The temperatures at which the isobaric curves intersect are indicated.

1. At constant pressure ΔT influences vapor more than a fluid
2. At modest pressures (0.1 and 1 MPa) liquids (and solids) insensitive to pressure.

4. Thermodynamic Efficiency:

For a closed system - no heat supply

$$\text{Efficiency} = \frac{w}{q_r} = \frac{\Delta \Phi}{q_o}$$

If no heat supply then write as temperatures

$$\text{Efficiency} = \frac{T_i - T_2}{T_i}$$

All temperatures in Kelvin!!

Thus - T_1 = initial temperature fluid
 T_2 = cooled fluid (say 290K).
 Efficiency \uparrow with temperature of geothermal fluid

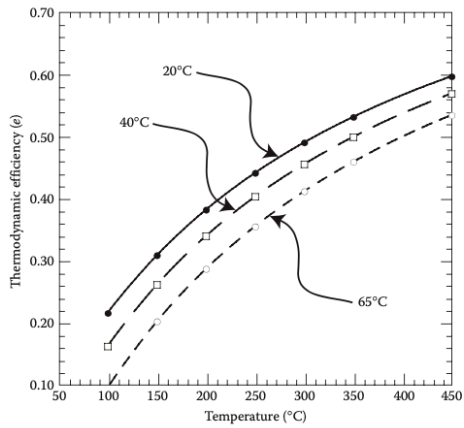


FIGURE 3.6 The thermodynamic efficiency that can be achieved for working fluids that begin at the temperature indicated on the horizontal axis and have an exit temperature as indicated by the arrowed lines. For example, a fluid that began at 200°C and had an exit temperature of 65°C would achieve an efficiency of 0.29, whereas that same fluid would achieve an efficiency of 0.39 if it had an exit temperature of 20°C.

TABLE 3.1
 Relationship between Temperatures and Efficiencies for Some Hypothetical Geothermal Reservoir Systems

| Reservoir | Reservoir Temperature (°C) | Cooled Temperature (°C) | Efficiency (e) |
|--|----------------------------|-------------------------|----------------|
| Low-temperature resource | 100 | 25 | 0.20 |
| Moderate-temperature resource (winter) | 200 | 10 | 0.40 |
| Moderate-temperature resource (summer) | 200 | 35 | 0.33 |
| High-temperature resource | 300 | 25 | 0.48 |
| High-temperature resource | 450 | 25 | 0.59 |

5. Thermodynamic Properties of Water and Water-Rock Interaction:

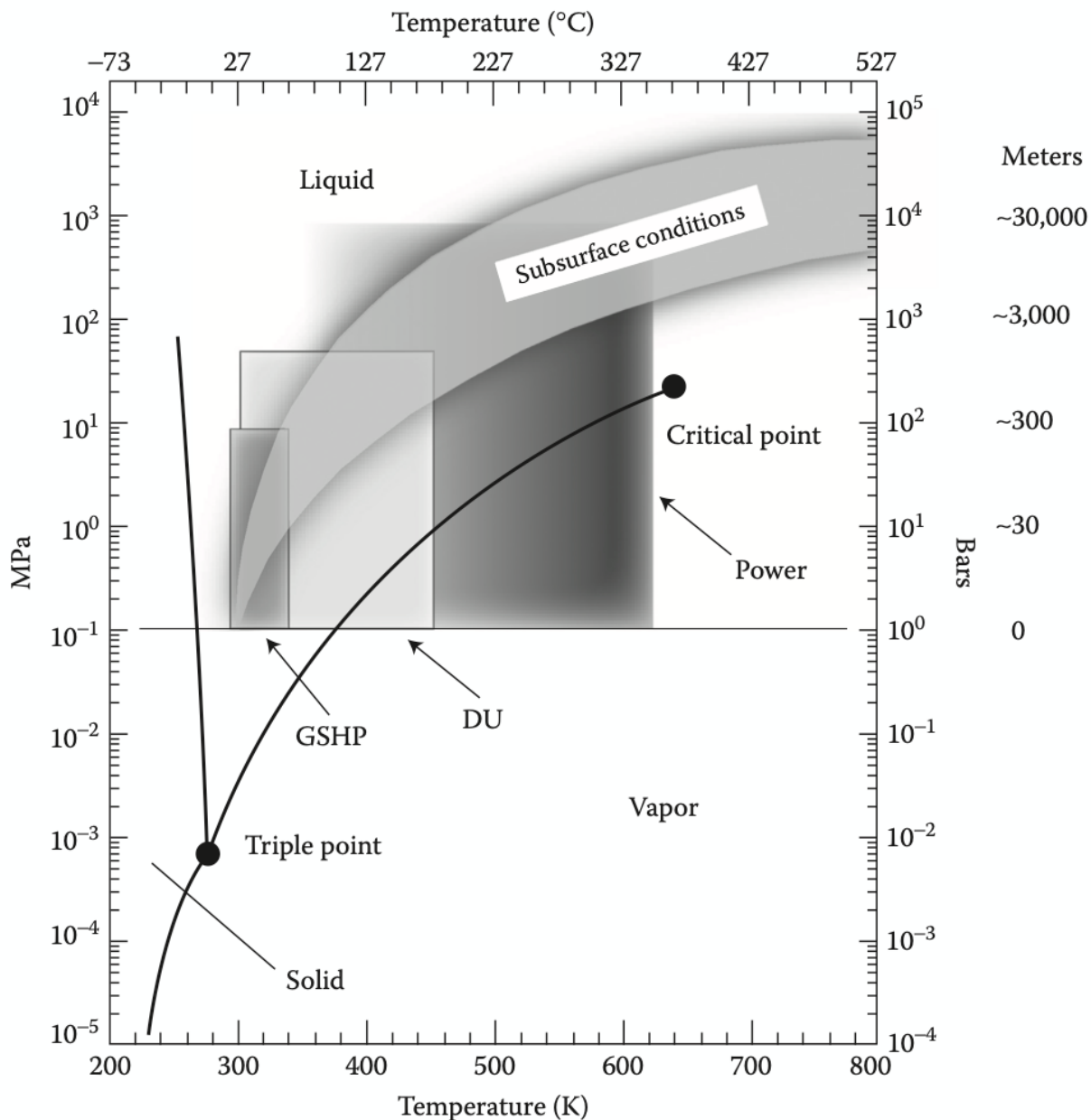


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent depth, in meters, below the earth's surface, for the corresponding pressures. The gray band indicates the range of pressure-temperature conditions encountered with depth in the earth. The shaded boxes enclose those sets of conditions appropriate for ground source heat pump applications (medium gray), direct-use applications (light gray), and power generation (gray gradient).

TABLE 3.2

Constant Pressure Heat Capacity (C_p) of Some Common Materials Important for Geothermal Applications at Atmospheric Pressure (1 bar) and 25°C (273 K) and 300°C (573 K); Units Are kJ/kg-K

| Material | 25°C, 1 bar | 300°C, 1 bar |
|---------------------------------|-------------|--------------|
| Water ^a | 4.18 | 2.01 |
| Air ^b | 1.00 | 1.04 |
| Potassium feldspar ^c | 0.66 | 1.05 |

Sources: ^aBowers, T.S., *Rock Physics and Phase Relations*, ed. T.J. Ahrens, American Geophysical Union, Washington, DC, 45–72, 1995.

^b Rabehl, R.J., *Parameter Estimation and the Use of Catalog Data with TRNSYS*. M.S. Thesis, Mechanical Engineering Department, University of Wisconsin-Madison, Madison, WI, 1997.

^c Helgeson, H. C. et al., *American Journal of Science*, 278-A, 229, 1978.

Energy recovered from water @ 25°C

$$Q = \underbrace{\rho C_p}_{\text{Mass}} \Delta T = M \cdot C_p \cdot \Delta T$$

So for $\Delta T = 1^\circ\text{C}$; $M = 1\text{kg} = 1\text{l}$;

$$Q = 1 \times 4180 \text{ J/kgK} \times 1\text{K} = \underline{4180\text{J}}$$

Total enthalpy is $H = M \cdot C_p \cdot T \uparrow^{25+273\text{K}}$

$$H = 1\text{kg} \times 4180 \text{ J/kg.K} \times 298\text{K}$$

$$\text{or } \sim Q \times 300$$

\therefore change in enthalpy

$$\sim \frac{1}{300} \sim 0.33\%$$

QED

PHASE CHANGE IN SYSTEMS

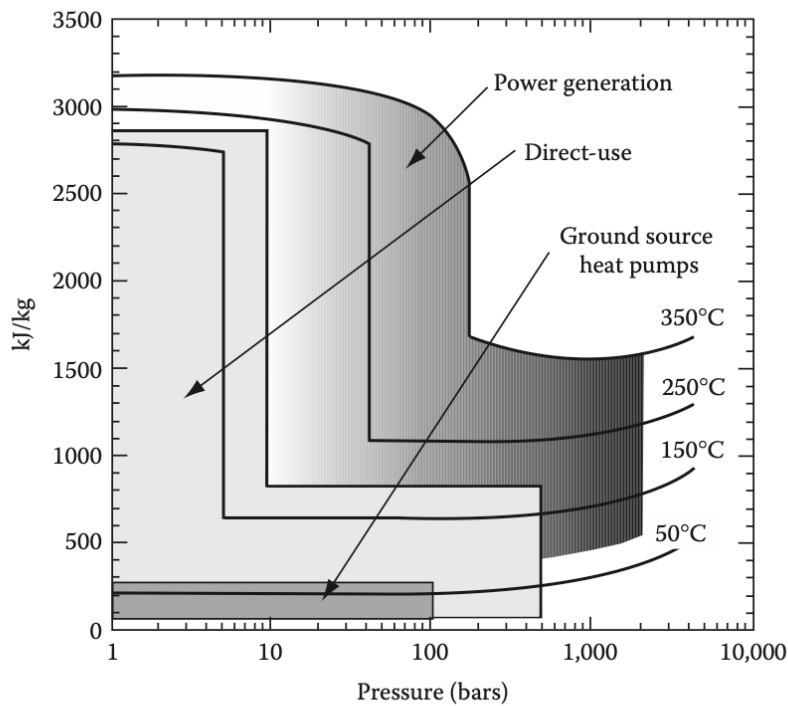


FIGURE 3.8 Enthalpy versus pressure diagram for water, with the corresponding regions for various geothermal applications, color coded as in Figure 3.7.

TABLE 3.3
Temperature, Pressure, and Enthalpy of Coexisting Steam and Vapor
along the Liquid-Vapor Saturation Curve

| Temperature (°C) | Pressure (bar) | Enthalpy (J/gm) of Vapor | Enthalpy (J/gm) of Liquid |
|------------------|----------------|--------------------------|---------------------------|
| 20 | 0.02 | 2538 | 83.96 |
| 25 | 0.03 | 2547 | 104.9 |
| 30 | 0.04 | 2556 | 125.8 |
| 35 | 0.06 | 2565 | 146.7 |
| 40 | 0.07 | 2574 | 167.6 |
| 45 | 0.10 | 2583 | 188.4 |
| 50 | 0.12 | 2592 | 209.3 |
| 55 | 0.16 | 2601 | 230.2 |
| 60 | 0.20 | 2610 | 251.1 |
| 65 | 0.25 | 2618 | 272.0 |
| 70 | 0.31 | 2627 | 293.0 |
| 75 | 0.39 | 2635 | 313.9 |
| 80 | 0.47 | 2644 | 334.9 |
| 85 | 0.58 | 2652 | 355.9 |
| 90 | 0.70 | 2660 | 376.9 |
| 95 | 0.85 | 2668 | 398.0 |
| 100 | 1.01 | 2676 | 419.0 |
| 110 | 1.43 | 2691 | 461.3 |
| 120 | 1.99 | 2706 | 503.7 |
| 130 | 2.70 | 2720 | 546.3 |
| 140 | 3.61 | 2734 | 589.1 |
| 150 | 4.76 | 2746 | 632.2 |
| 160 | 6.18 | 2758 | 675.5 |
| 170 | 7.92 | 2769 | 719.2 |
| 180 | 10.02 | 2778 | 763.2 |
| 190 | 12.54 | 2786 | 807.6 |
| 200 | 15.54 | 2793 | 852.4 |
| 210 | 19.06 | 2798 | 897.8 |
| 220 | 23.18 | 2802 | 943.6 |
| 230 | 27.95 | 2804 | 990.1 |
| 240 | 33.44 | 2804 | 1037.00 |
| 250 | 39.73 | 2802 | 1085.00 |
| 260 | 46.89 | 2797 | 1134.00 |
| 270 | 54.99 | 2790 | 1185.00 |
| 280 | 64.12 | 2780 | 1236.00 |
| 290 | 74.36 | 2766 | 1289.00 |
| 300 | 85.81 | 2749 | 1344.00 |
| 310 | 98.56 | 2727 | 1401.00 |
| 320 | 112.70 | 2700 | 1461.00 |
| 330 | 128.40 | 2666 | 1525.00 |
| 340 | 145.80 | 2622 | 1594.00 |
| 350 | 165.10 | 2564 | 1671.00 |

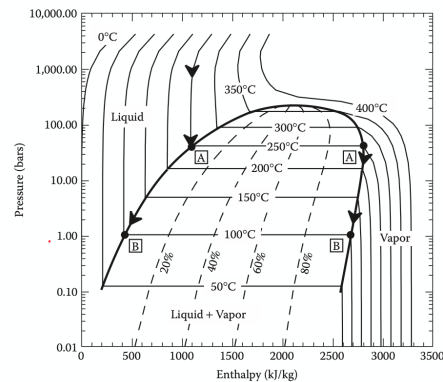


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure-enthalpy path followed by a liquid at 250°C that ascends from 1000 bars and exits a wellhead at 1 bar and 100°C.

PHASE CHANGE

- ① Largest energy recovery with phase change
- ② Rapid recovery of hot water at depth
→ Δp but $\Delta h = 0$

Conservation:

1. Mass $\Delta M = 0$
2. Enthalpy $\Delta H = 0$

Example: Water @ 250°C
 $p = 40 \text{ bar @ } 1500 \text{ m}$
(4 MPa)

$$H_{1,250^\circ\text{C}} = x \times H_{1,100^\circ\text{C}} + (1-x) \times H_{v,100^\circ\text{C}}$$

where:

the subscripts l and v stand for liquid and vapor, respectively
 x is the fraction of the mass of the system that is liquid

Enthalpies: liquid @ $250^\circ\text{C} / 40 \text{ bar} = 1.085 \text{ J/kg}$
 $100^\circ\text{C} / 1 \text{ bar} = 0.419 \text{ J/kg}$
Vapor @ $100^\circ\text{C} / 1 \text{ bar} = 2.676 \text{ J/kg}$

Solve for liquid fraction " x ."

$$x \sim 70\% \quad \text{and} \quad 1-x \sim 30\%$$

3. For Each Sub-Topic:

a. **Detailed Explanation of the Topic [40%]** Describe the physical principles in detail and at a pace that is tutorial for an audience.

Summary - in terms of EME 303

First law of thermodynamics (Conservation of energy)
$$\frac{\partial}{\partial t} \int_{cv} e \rho dV + \int_{cs} \left(\check{u} + \frac{p}{\rho} + \frac{V^2}{2} + gz \right) \rho \mathbf{V} \cdot \hat{\mathbf{n}} dA = \dot{Q}_{\text{net in}} + \dot{W}_{\text{shaft net in}} \quad (5.64)$$

Conservation of power
$$\dot{m} \left[\check{h}_{\text{out}} - \check{h}_{\text{in}} + \frac{V_{\text{out}}^2 - V_{\text{in}}^2}{2} + g(z_{\text{out}} - z_{\text{in}}) \right] = \dot{Q}_{\text{net in}} + \dot{W}_{\text{shaft net in}} \quad (5.69)$$

Conservation of mechanical energy
$$\frac{p_{\text{out}}}{\rho} + \frac{V_{\text{out}}^2}{2} + gz_{\text{out}} = \frac{p_{\text{in}}}{\rho} + \frac{V_{\text{in}}^2}{2} + gz_{\text{in}} + w_{\text{shaft net in}} - \text{loss} \quad (5.82)$$

b. **Example Hand-Calculation [10%]** Simple calculation to demonstrate the technique.

c. **Case Study [10%]** If appropriate.

Conclusion:

4. **Conclusion [20%]** Summarize important/key points from the presentation.