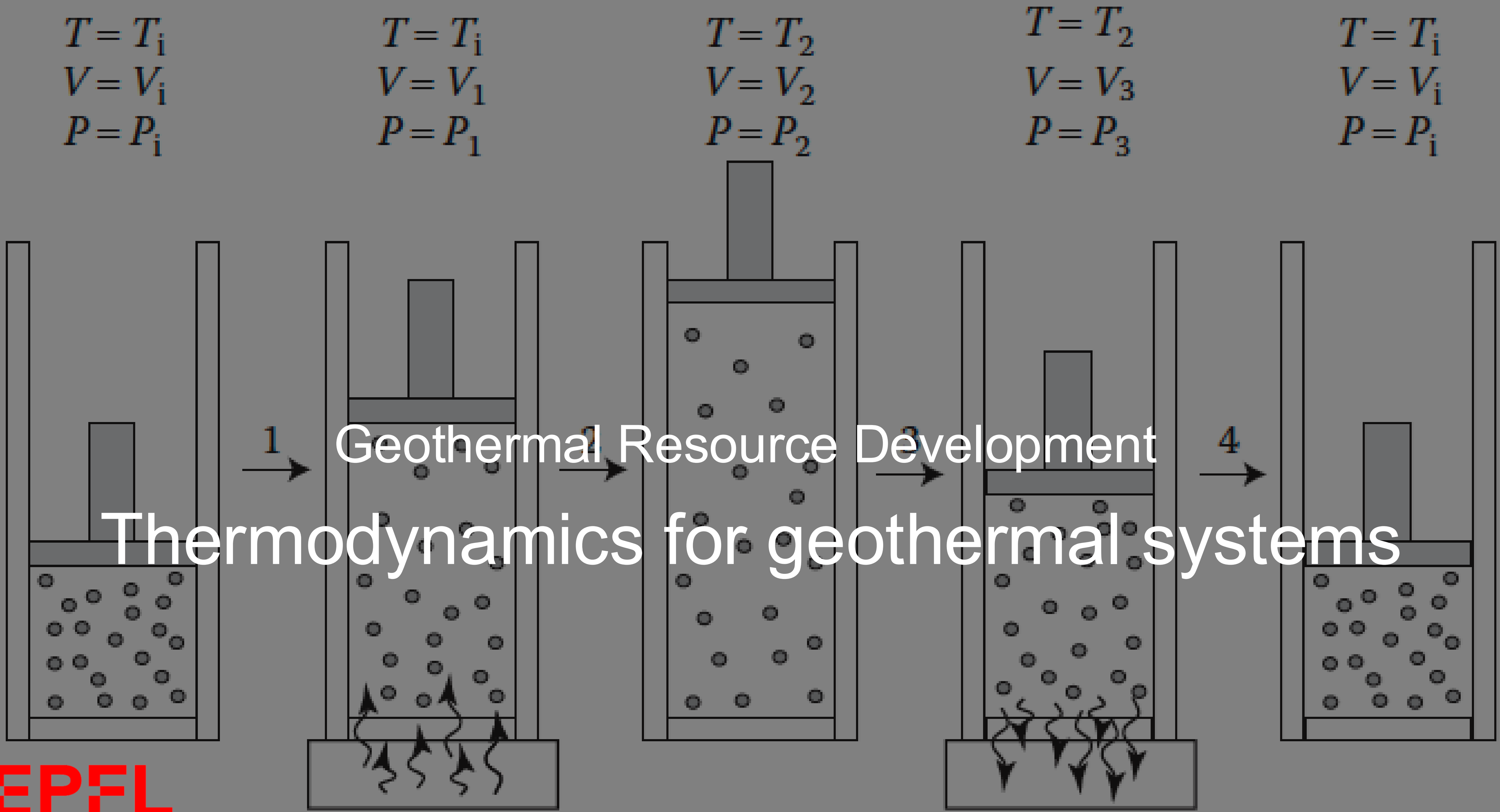
Geothermal Resource Development

Thermodynamics for geothermal systems



Geothermal energy use

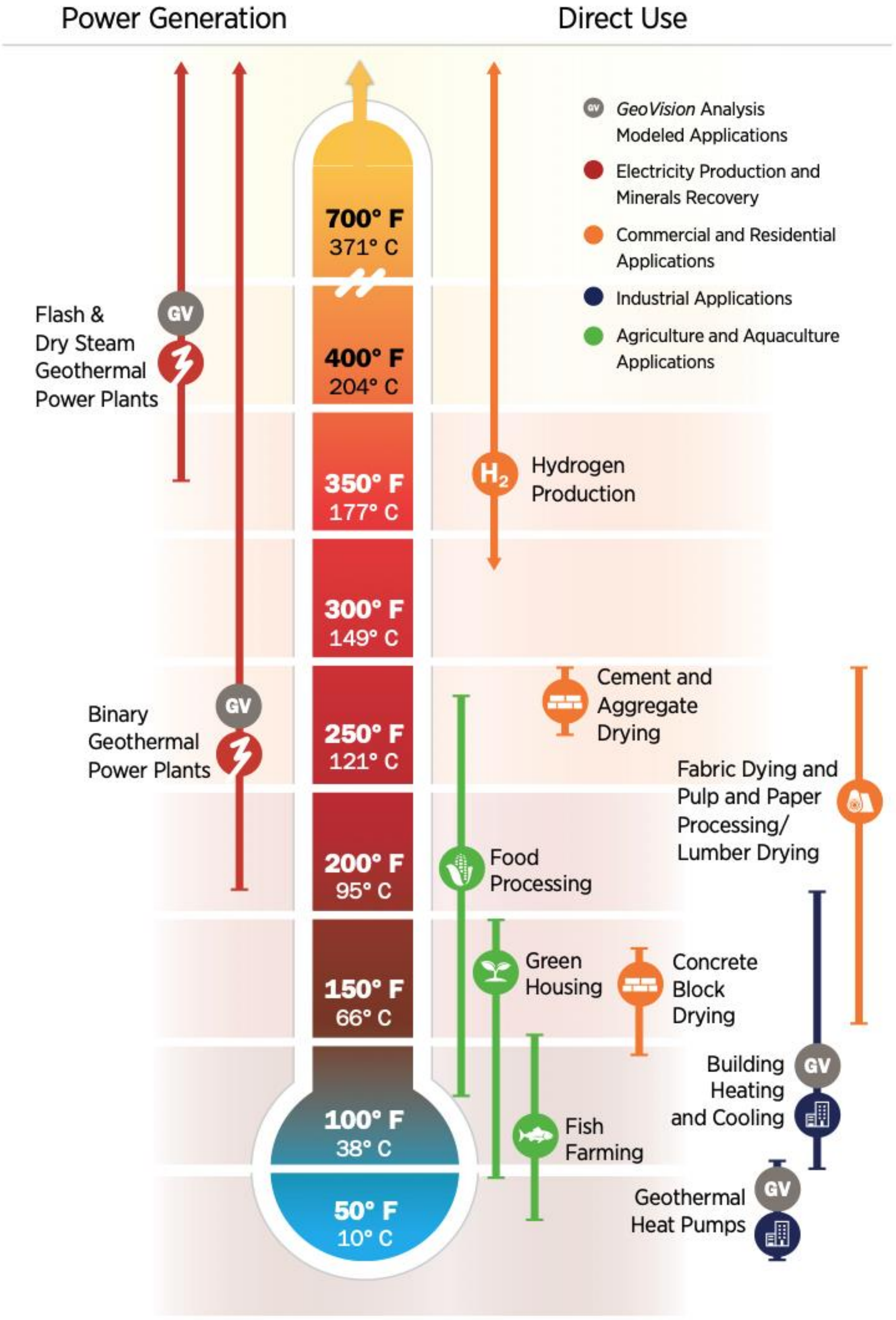
Geothermal energy mines heat to do work.

How do we move heat and convert it to work?

How do fluids and materials behave when heated and cooled?

How does this affect the energy balance of geothermal systems?

We need to understand the **thermodynamics** of geothermal systems.



Source: US Department of Energy, *U.S. GeoVision report, Chapter 2, p. 14*

Topics covered today...

1. First law of thermodynamics
2. The Carnot Cycle
3. Second law of thermodynamics
4. Work and heat capacity
5. Gibbs function and Gibbs energy
6. Thermodynamic efficiency

First law of thermodynamics:

Energy is conserved: mechanical work and heat are equivalent.

A system and its internal energy

System: Anything that can be described by parameters of state.

- Temperature
- Pressure
- Volume

Closed system: A system that is completely isolated from its surroundings such that no mass can move in or out of it.

- At any given set of conditions (P,T), the internal energy (E) is fixed and depends only on the properties of the materials of which the system is composed
- E changes in response to changes in P and T
- If heat (Q) is moved or work (w) is done, the internal energy (E) will change.

First law of thermodynamics

Any change in internal energy (E) of a system is solely the result of the work (*w*) done on or performed by the system, and any heat (*Q*) added to or removed from the system.

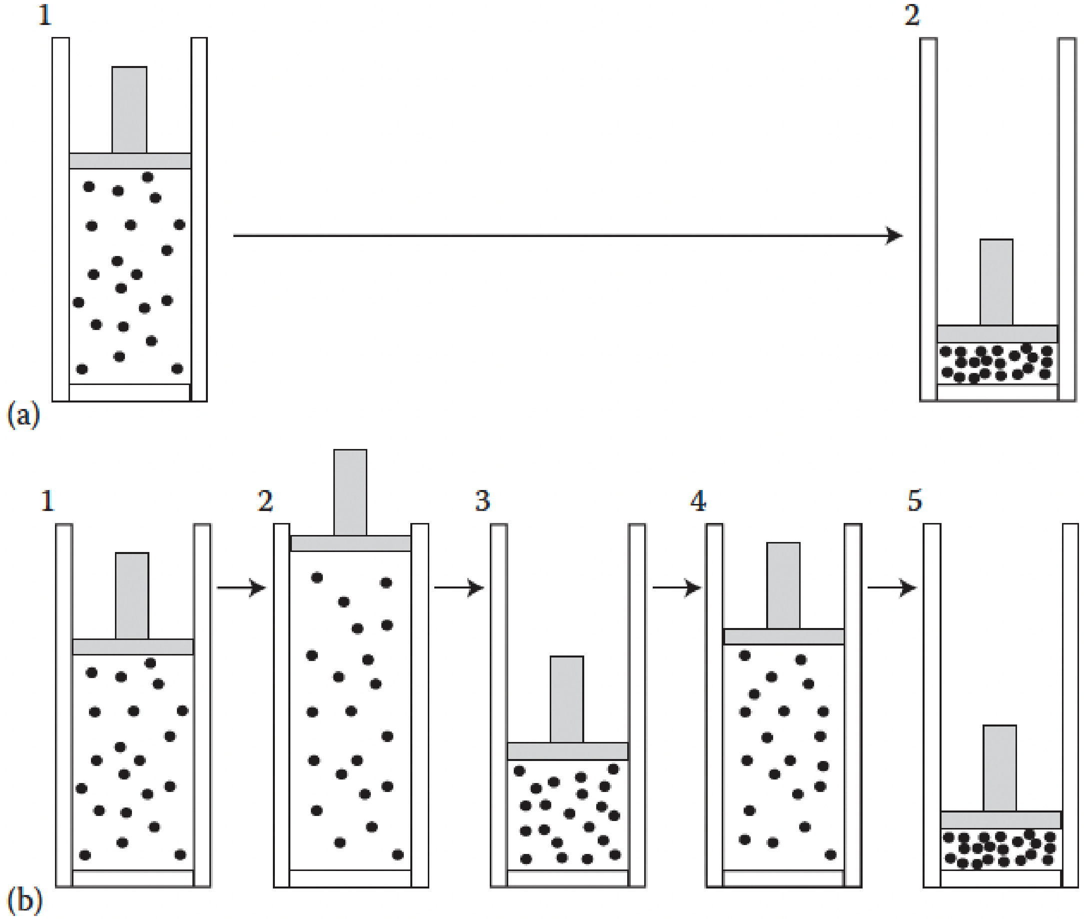
$$\Delta E = Q + w$$

ΔE – change in energy in the system

Q – amount of energy added or removed from the system as heat

w - amount of work done on the system

A system and its internal energy



Source: Glassley, W. E., *Geothermal Energy*

A system and its internal energy

$$\Delta E = E_f - E_i$$

ΔE – the change in internal energy

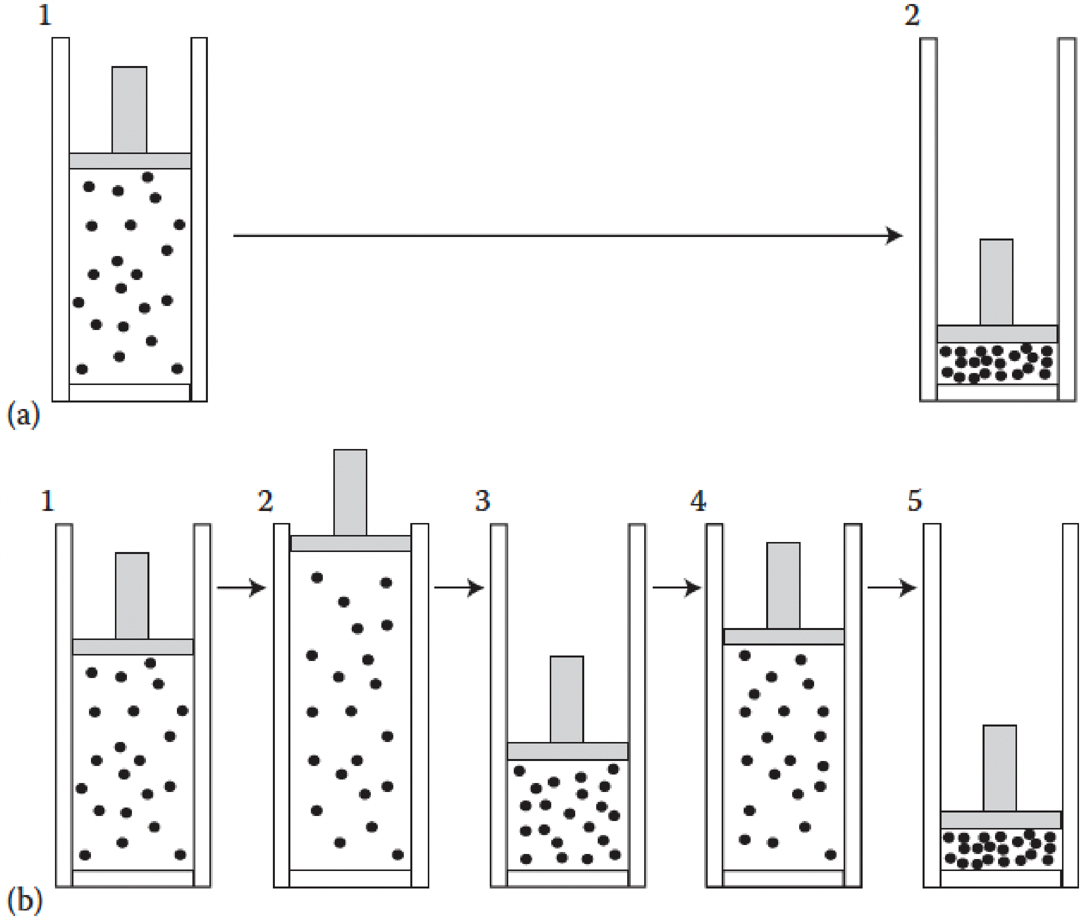
E_f – the energy of the system in its final state

E_i – is the initial internal energy

Simple, but critical.

You need to know E_f and E_i if you want to know how much energy is required to do something.

The pathway to get from E_i to E_f does not matter.



Source: Glassley, W. E., *Geothermal Energy*

Pressure-volume work

Mechanical work: when a force is applied to a point, surface, or volume and results in displacement of that point, surface, or volume.

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

P – pressure in the system

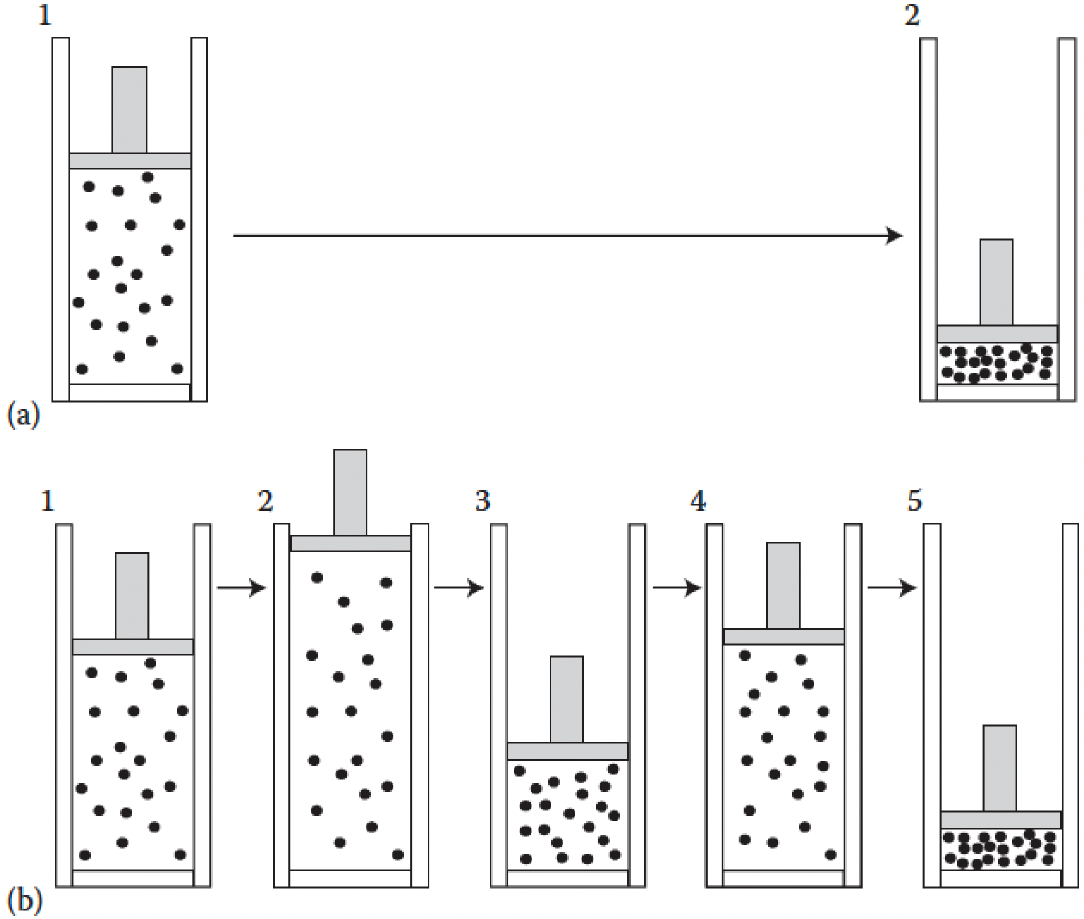
V_1 – initial volume of the system

V_2 – final volume of the system

ΔV – change in volume of the system

Convention:

- Mechanical work done *on* a system is positive
- Mechanical work done *by* a system is negative



Source: Glassley, W. E., *Geothermal Energy*

Enthalpy

When no mechanical work (*w*) occurs (and therefore no ΔV), changes in internal energy (ΔE) is due only to changes in heat (Q):

$$\Delta E = Q_v$$

(subscipt *v* denotes that the system has constant volume)

Enthalpy

When no mechanical work (*w)* occurs (and therefore no ΔV), changes in internal energy (ΔE) is due only to changes in heat (Q):

$$\Delta E = Q_v$$

(subscipt *v* denotes that the system has constant volume)

If volume changes, but pressure is constant, AND heat is added/removed to/from the system:

$$\Delta E = Q_p - (P \times \Delta V)$$

Or

$$\Delta E = Q_p + w$$

(subscipt *p* denotes that the system has constant pressure)

Enthalpy

When no mechanical work (*w)* occurs (and therefore no ΔV), changes in internal energy (ΔE) is due only to changes in heat (*Q*):

$$\Delta E = Q_v$$

(subscipt *v* denotes that the system has constant volume, w = 0)

If volume changes, but pressure is constant, AND heat is added/removed to/from the system:

$$\Delta E = Q_p - (P \times \Delta V)$$

(subscipt *p* denotes that the system has constant pressure, w = $-P \times \Delta V$)

Enthalpy *(H)*: The heat added to or removed from the system at constant pressure.

Change in enthalpy is defined:

$$\boldsymbol{\Delta H = [E_2 + (P \times V_2)] - [E_1 + (P \times V_1)] = Q_p}$$

Enthalpy

Enthalpy *(H)*: The heat added to or removed from the system at constant pressure. Change is enthalpy is defined:

$$\Delta H = [E_2 + (P \times V_2)] - [E_1 + (P \times V_1)] = Q_p$$

Units: J/kg

Enthalpy gives us a way to establish the behaviour of a system in the subsurface and allows for evaluation of the useful energy that can be extracted from a working fluid.

Week 8: Generating power using geothermal

Efficiency

How much work can be done for a given amount of heat?

Efficiency is a measure of what proportion of heat can be used to do work.

100% efficiency: all the energy contained in a given amount of heat can be used to do work.

Mathematically, efficiency (*e*) of any situation involving heat and work is given:

$$e = -\frac{w}{Q}$$

100% efficiency: $Q = -w$ and $e = 1.0$

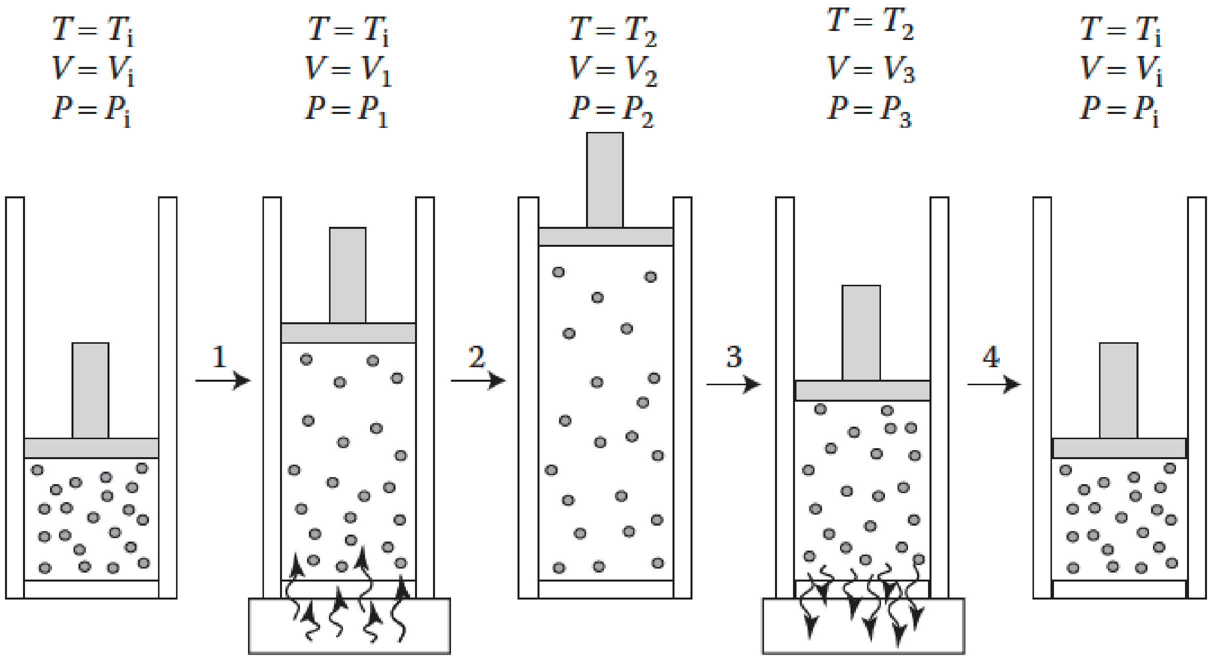
The Carnot Cycle

Carnot cycle

Thought experiment to conceptually model efficiency: idealised (imaginary) engine that cycles through 4 steps to convert heat to mechanical work.

Recall:

$$\Delta E = Q + w$$

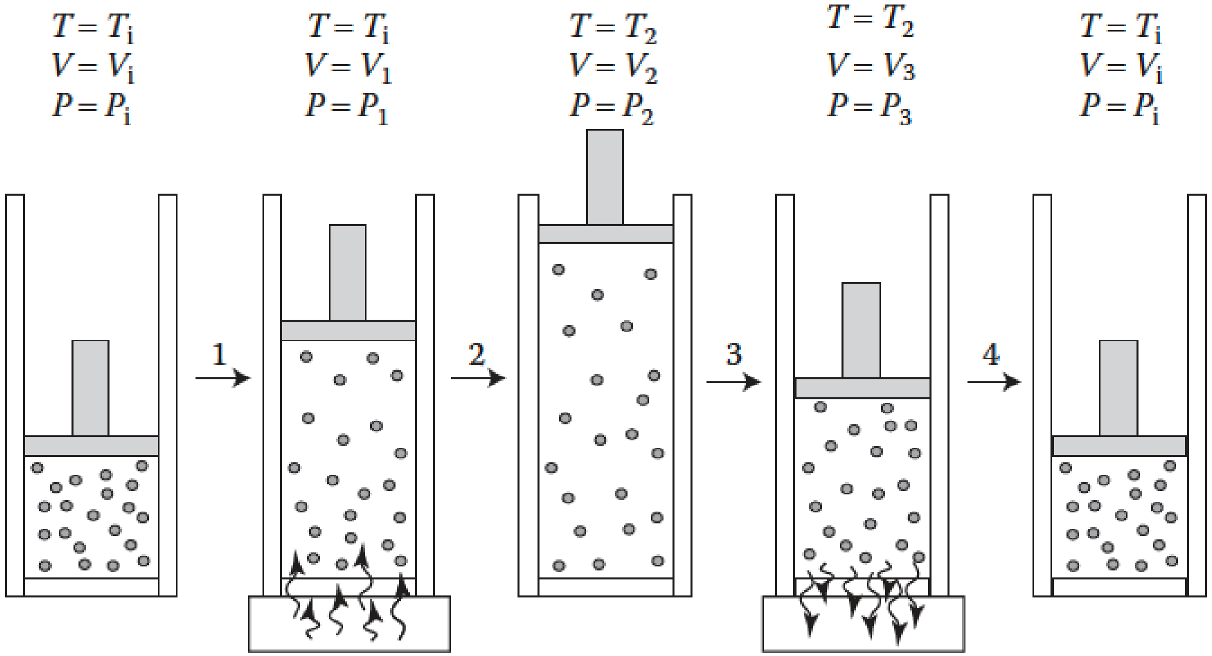


Source: Glassley, W. E., *Geothermal Energy*

Carnot cycle

Assumptions:

1. We do not consider how the system came to its initial state
2. At the end of the 4th cycle, the engine returns to its initial state.
   - ΔP, ΔT, and $\Delta V = 0$
   - $\Delta E = 0$
3. Each step is reversible: equilibrium is achieved continuously throughout each step.



Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

In its simplest form, the engine is a gas-filled cylinder with a frictionless piston.

The gas obeys the Ideal Gas Law:

$$PV = nRT$$

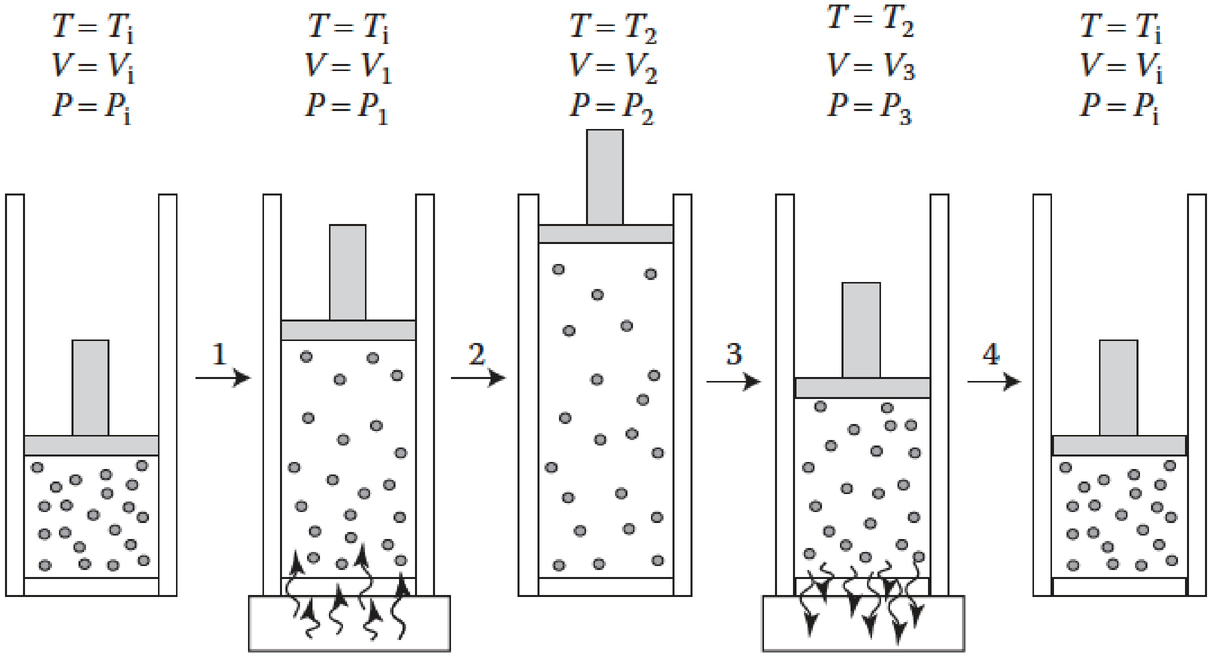
P – pressure

V – volume

n – moles of gas

T – temperature of the gas

R – universal gas constant (8.314 J/mol.K)



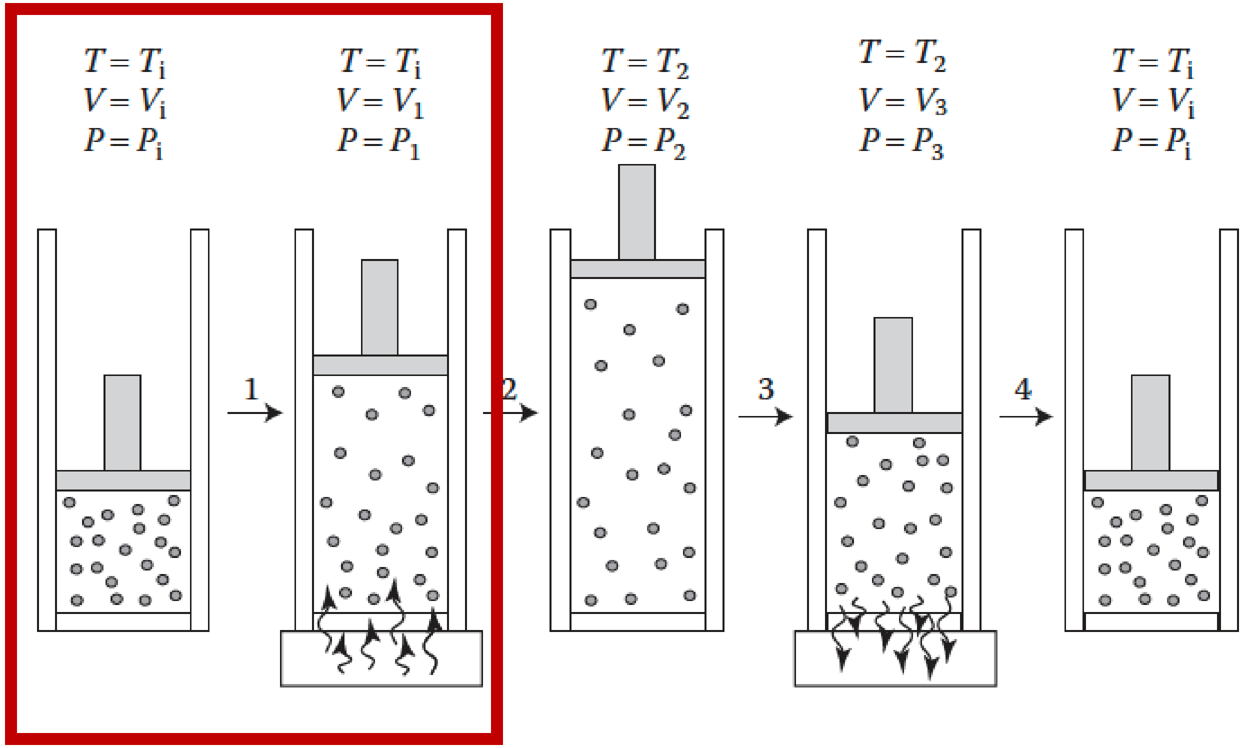
Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

Step 1: Add heat (Q) to the system from an external reservoir, as work is done on the gas.

- ***Isothermal expansion (T is constant)***
- *V* increases
- *P* decreases

$$\Delta E_1 = 0 = Q_1 + w_1$$



Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

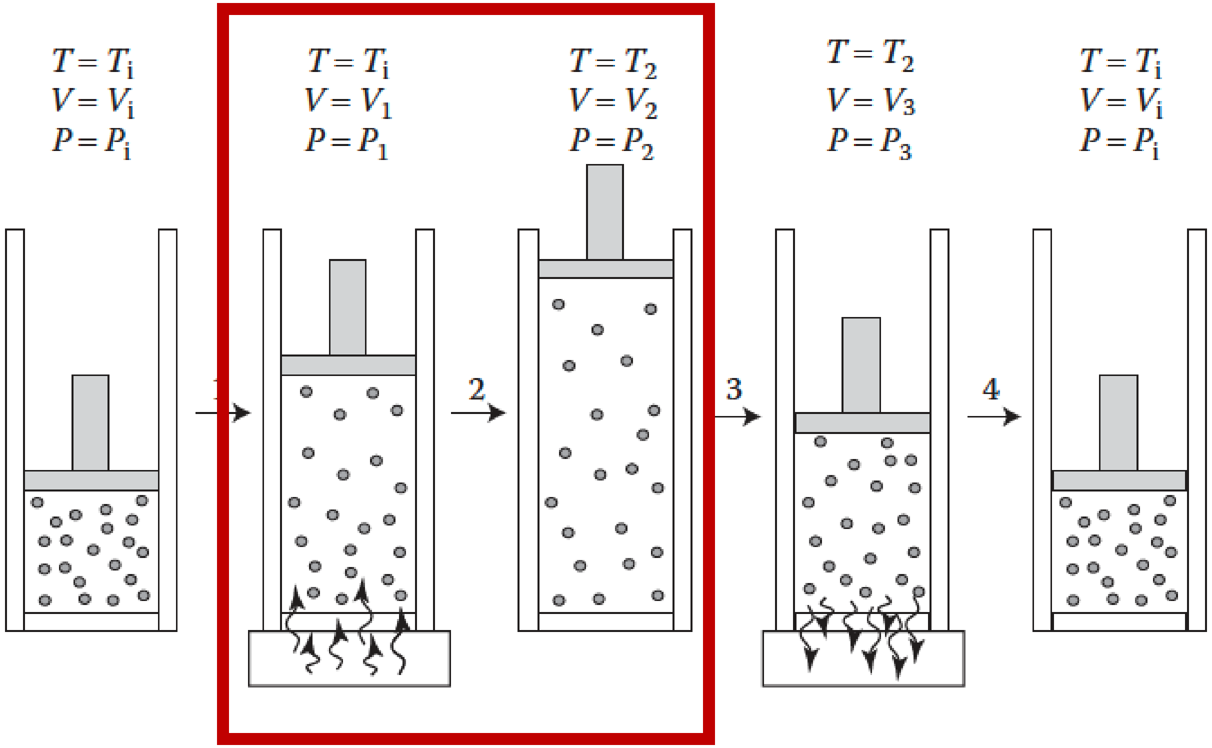
Step 1: Add heat (Q) to the system from an external reservoir, as work is done on the gas.

- ***Isothermal expansion (T is constant)***
- *V* increases
- *P* decreases

Step 2: Work is done on the gas without adding heat, to reduce gas T.

- ***Adiabatic expansion (Q = 0)***
- *V* increases
- *P* decreases
- *T decreases*

$$\Delta E_2 = 0 + w_2$$



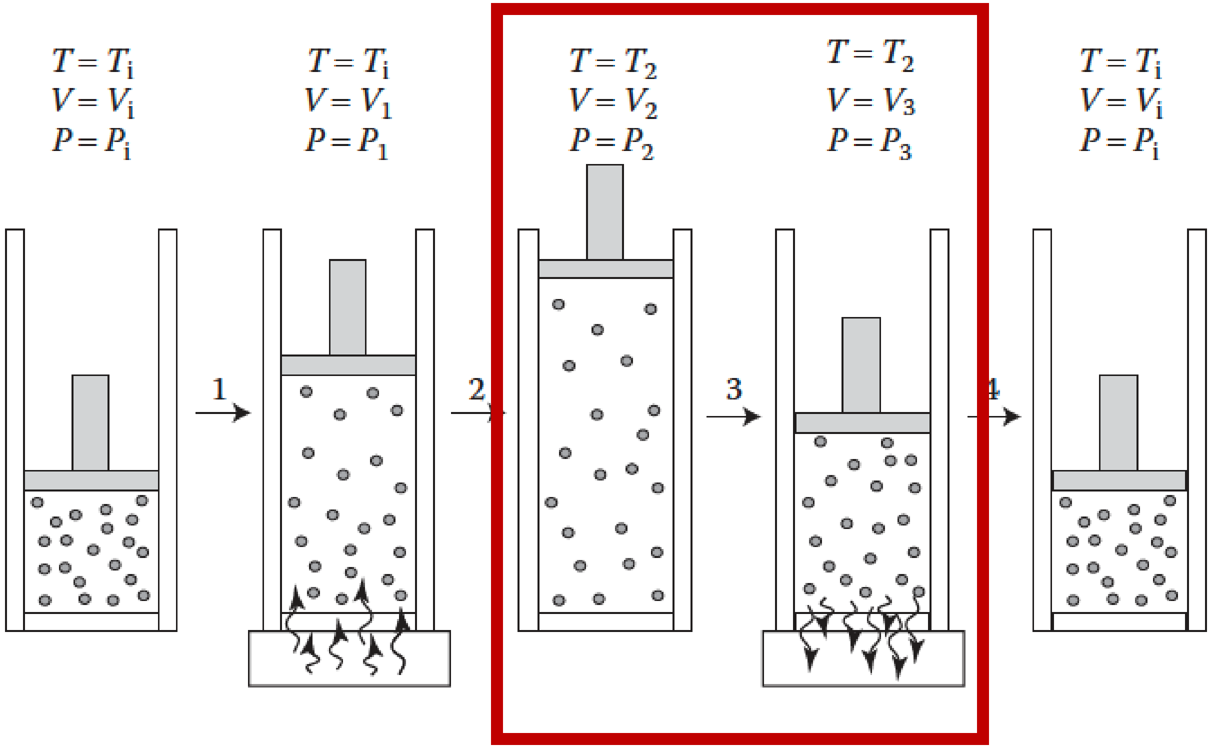
Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

Step 3: Remove heat from the system and put it in an external reservoir, as work is done by the gas.

- ***Isothermal compression (T is constant)***
- *V* decreases
- *P* increases

$$\Delta E_3 = 0 = -Q_3 - w_3$$



Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

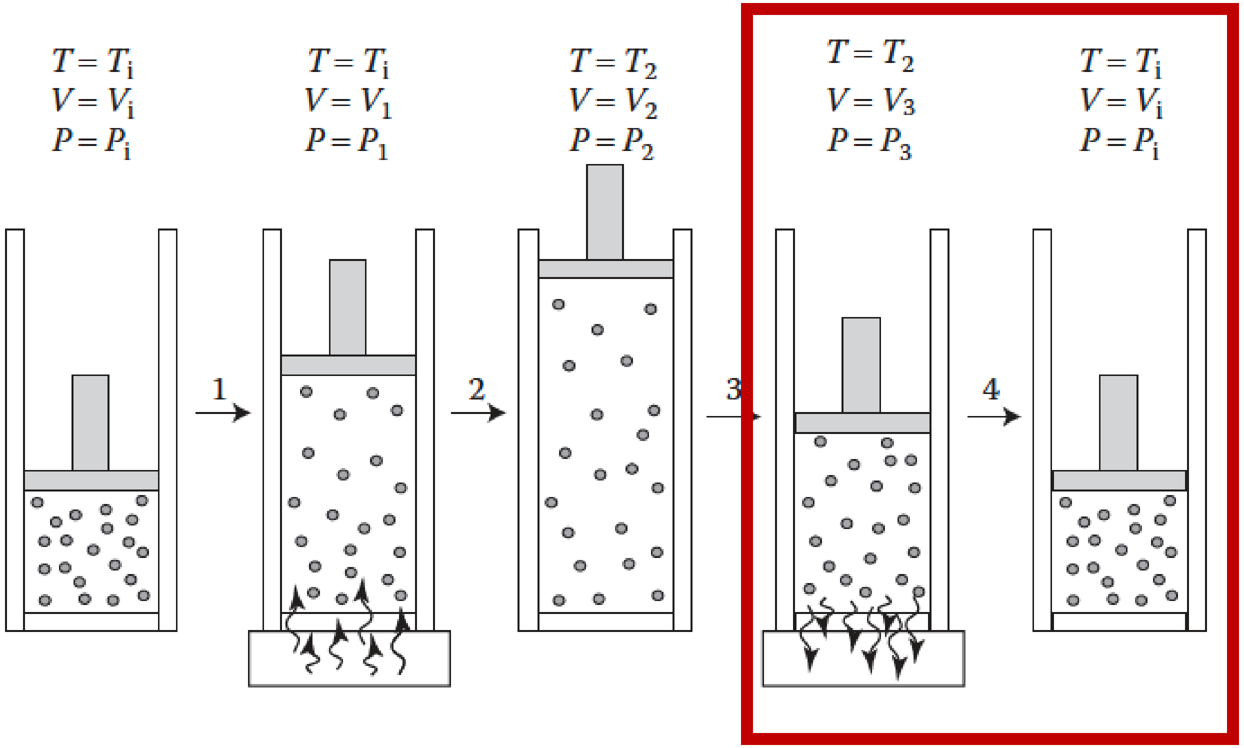
Step 3: Remove heat from the system and put it in an external reservoir, as work is done by the gas.

- ***Isothermal compression (T is constant)***
- *V* decreases
- *P* increases

Step 4: Work is done by the system, without adding heat, to increase gas T.

- ***Adiabatic compression***
- *V* decreases to initial value
- *P* increases to initial value
- *T* increases to initial value

$$\Delta E_4 = 0 - w_4$$



Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

Step 1: Isothermal expansion

- Add heat to the system.
- Heat converted to work.

Step 2: Adiabatic expansion

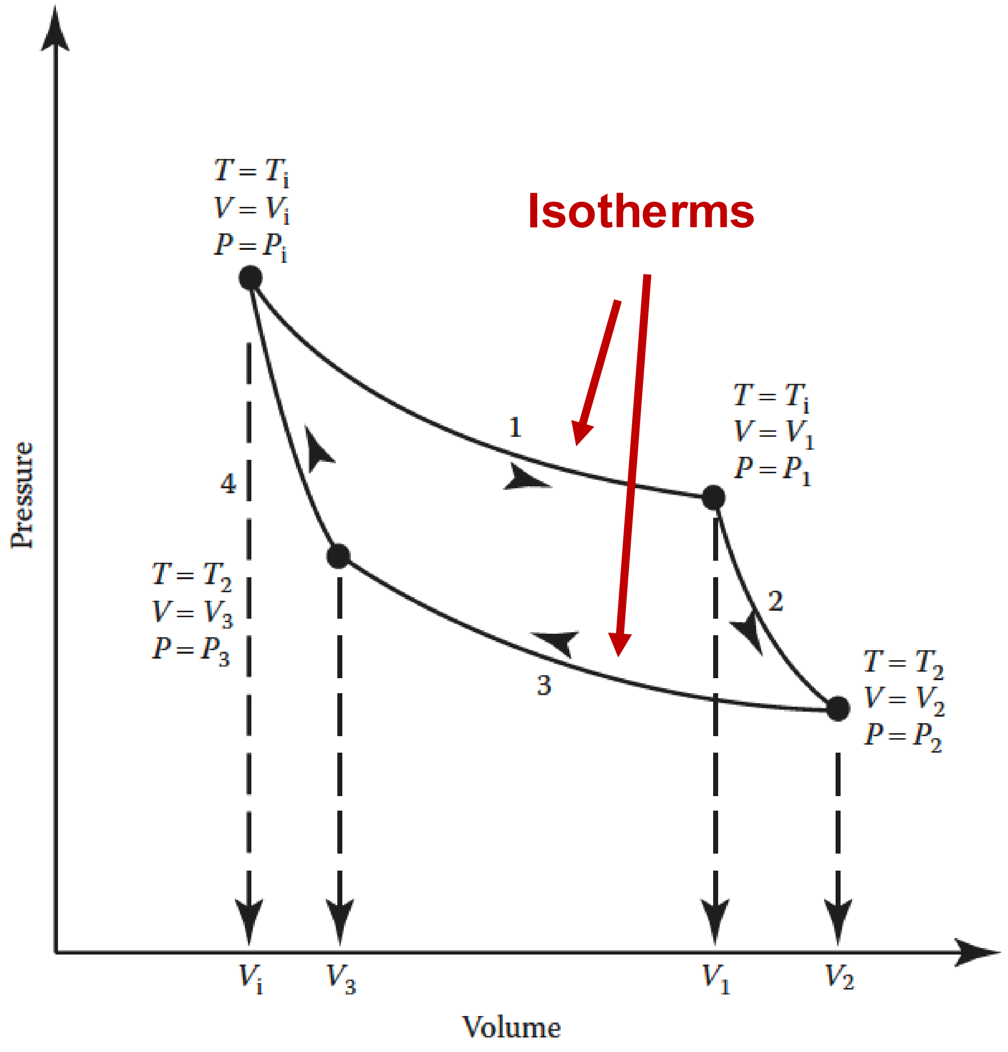
- Work is done on the system (to reduce T) without adding heat.

Step 3: Isothermal compression

- Remove heat from the system.
- Heat converted to work.

Step 4: Adiabatic compression

- Work is done by the the system (to increase T) without adding heat.



Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

What is the net work done by our Carnot engine?

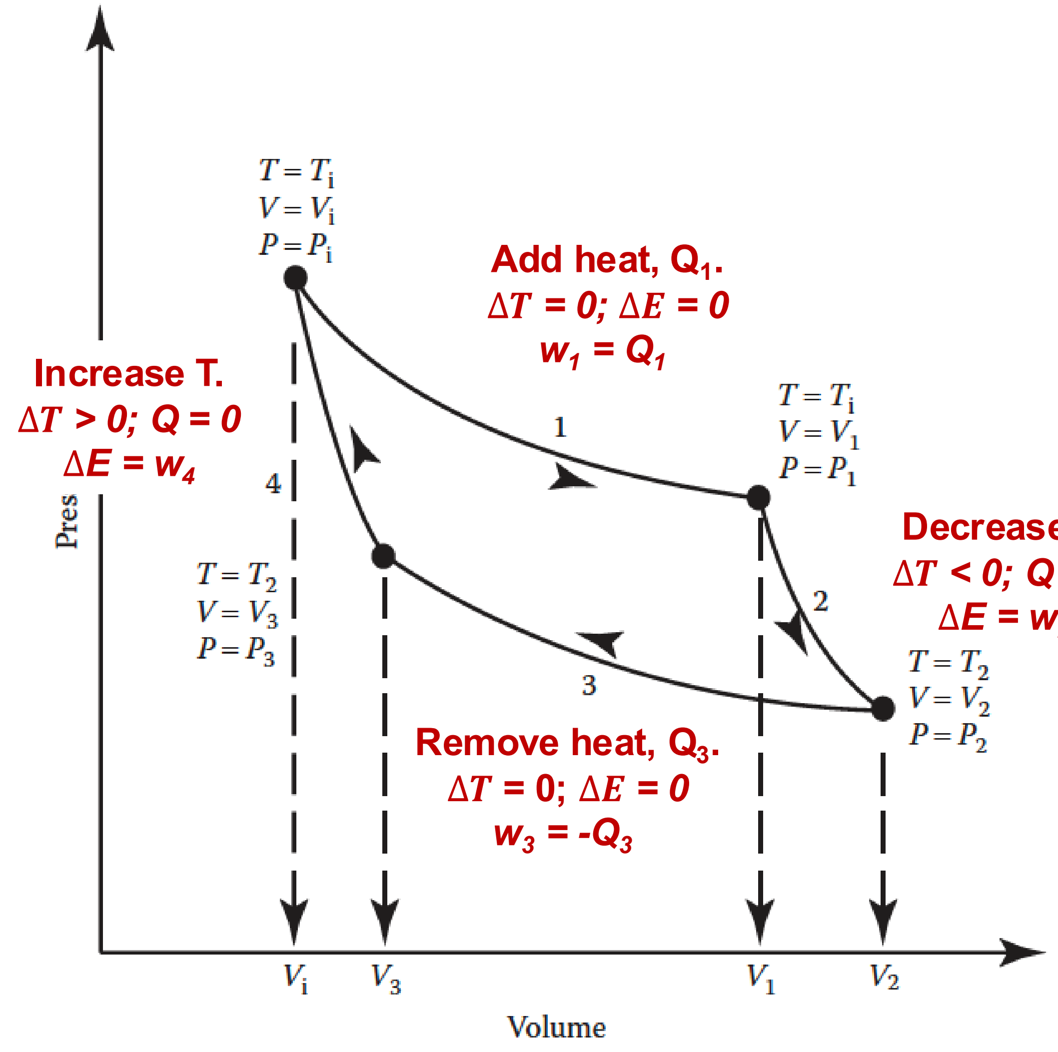
Recall:

$\Delta E = 0$ for a complete cycle.

Therefore: $w = Q$

And

$w = Q_1 - Q_3$



Add heat, Q_1.
$\Delta T = 0$; $\Delta E = 0$
$w_1 = Q_1$

Decrease T.
$\Delta T < 0$; $Q = 0$
$\Delta E = w_2$

Remove heat, Q_3.
$\Delta T = 0$; $\Delta E = 0$
$w_3 = -Q_3$

Increase T.
$\Delta T > 0$; $Q = 0$
$\Delta E = w_4$

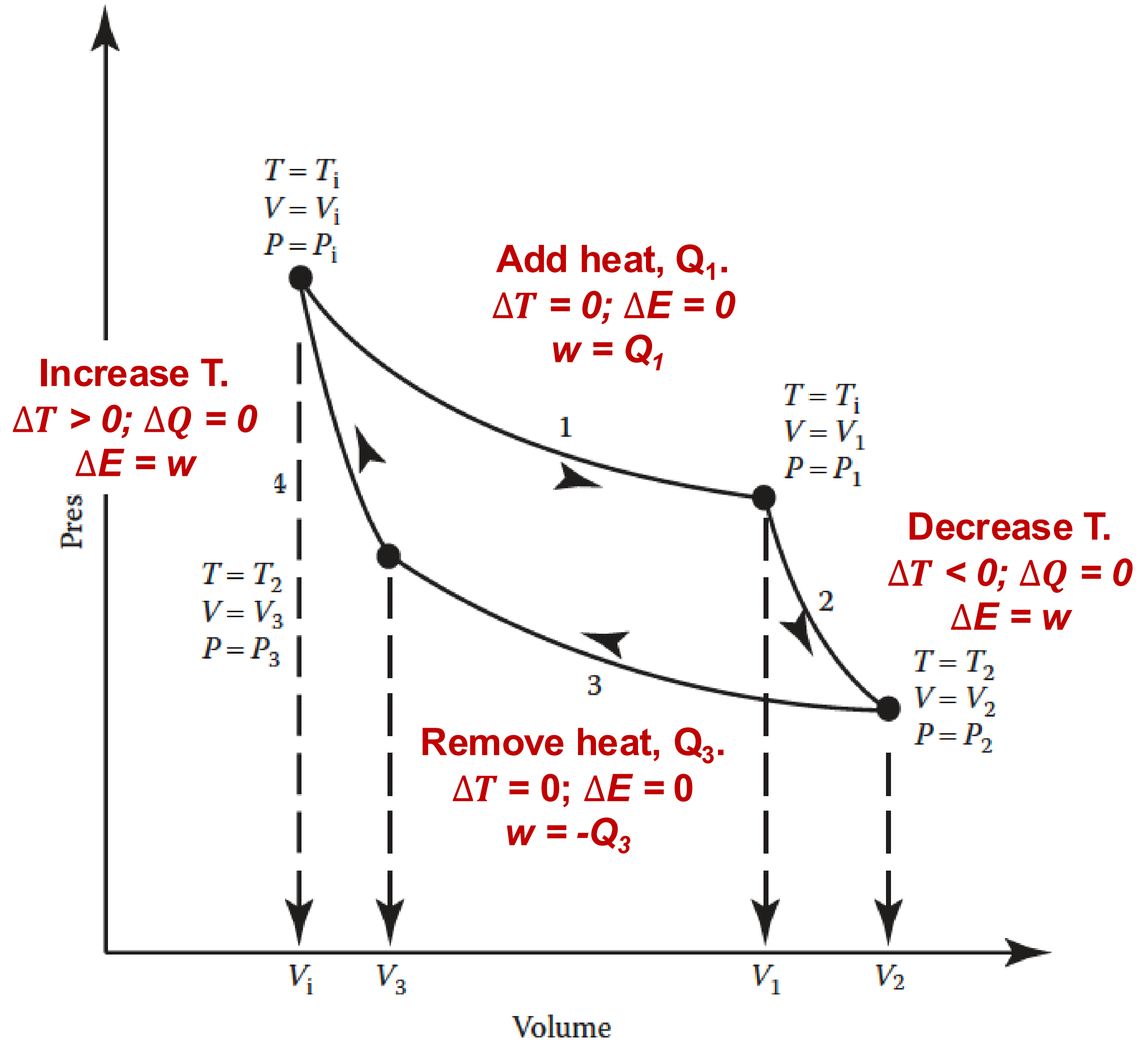
Source: Glassley, W. E., *Geothermal Energy*

Carnot engine

Efficiency of the engine is related to the amount of heat converted to work:

$$e = -\frac{w}{Q_{in}} = \frac{\Delta Q}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}}$$

100% efficiency (e = 1.0) occurs when no heat is returned to the cold reservoir in step 3 (i.e. all heat is converted to work) and the system returns to its original state.



Add heat, Q_1.
$\Delta T = 0; \Delta E = 0$
$w = Q_1$

Decrease T.
$\Delta T < 0; \Delta Q = 0$
$\Delta E = w$

Remove heat, Q_3.
$\Delta T = 0; \Delta E = 0$
$w = -Q_3$

Increase T.
$\Delta T > 0; \Delta Q = 0$
$\Delta E = w$

Source: Glassley, W. E., *Geothermal Energy*

Second law of thermodynamics:

The entropy of a system inevitably increases.

Entropy

In the Carnot cycle:

- The heat content at the beginning of the cycle does not get used to do work and we never access it
- The system is entirely reversible: we lose no heat…

Entropy

In the Carnot cycle:

- The heat content at the beginning of the cycle does not get used to do work and we never access it
- The system is entirely reversible: we lose no heat…

In real life, we also lose heat through friction and conduction: this heat is not "useful"

Entropy (S) is the measure of this unattainable heat (both the heat of the initial system AND the heat lost to processes involved in moving through the cycle, which is not used for work).

$$S \equiv \frac{dQ}{T}$$

Entropy in the Carnot Cycle

$$S \equiv \frac{dQ}{T}$$

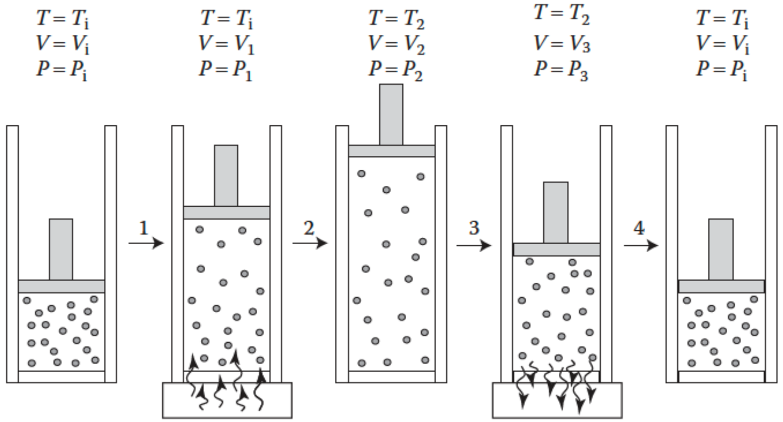
At a given temperature, the differential change in heat of the system results in change in entropy of the system:

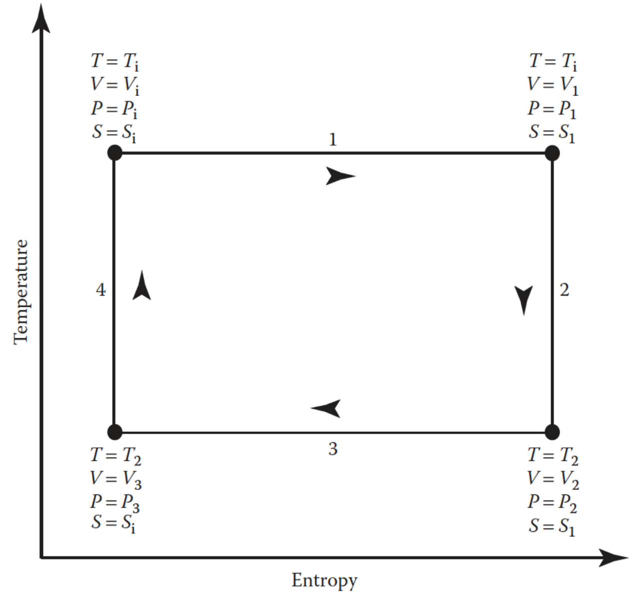
Step 1: *S* increases because heat is added to the system at constant *T*

Step 2: *T* decreases but there is no change in *Q*, so *dQ* = 0 and *S* does not change

Step 3: isothermal compression, *S* decreases because heat is removed from the system at constant *T*

Step 4: adiabatic compression, *T* increases but there is no change in *Q*, so *dQ* = 0 again





Source: Glassley, W. E., *Geothermal Energy*

Entropy in the Carnot Cycle

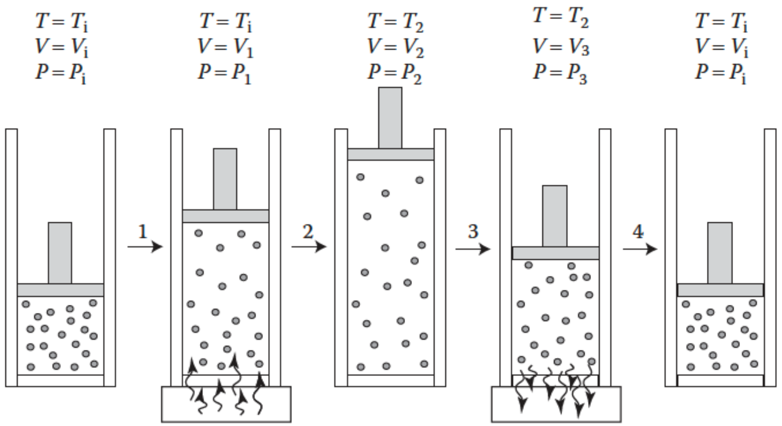
In reality, entropy increases: heat was added to and removed from the system using external heat reservoirs.

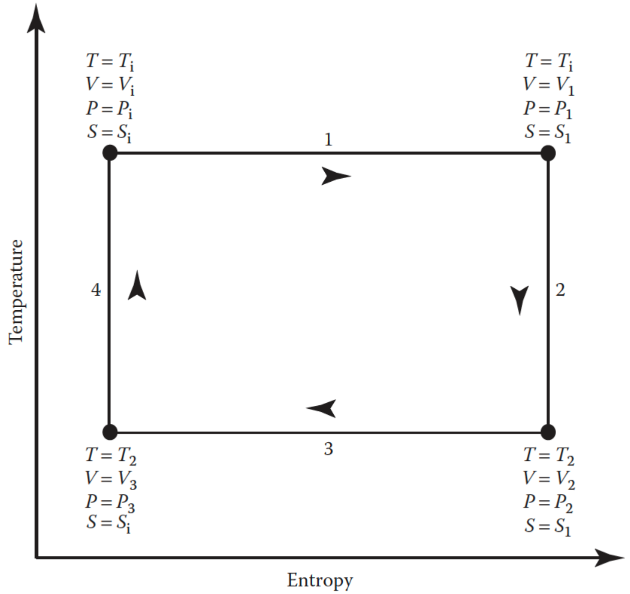
The high temperature reservoir loses heat.

The low temperature reservoir gains heat.

Over time, the two reservoirs approach the same temperature and the Carnot cycle ceases (*e = 0*) and *S* reaches a maximum.

No more work is possible.





Source: Glassley, W. E., *Geothermal Energy*

Work and heat capacity

Geothermal energy use

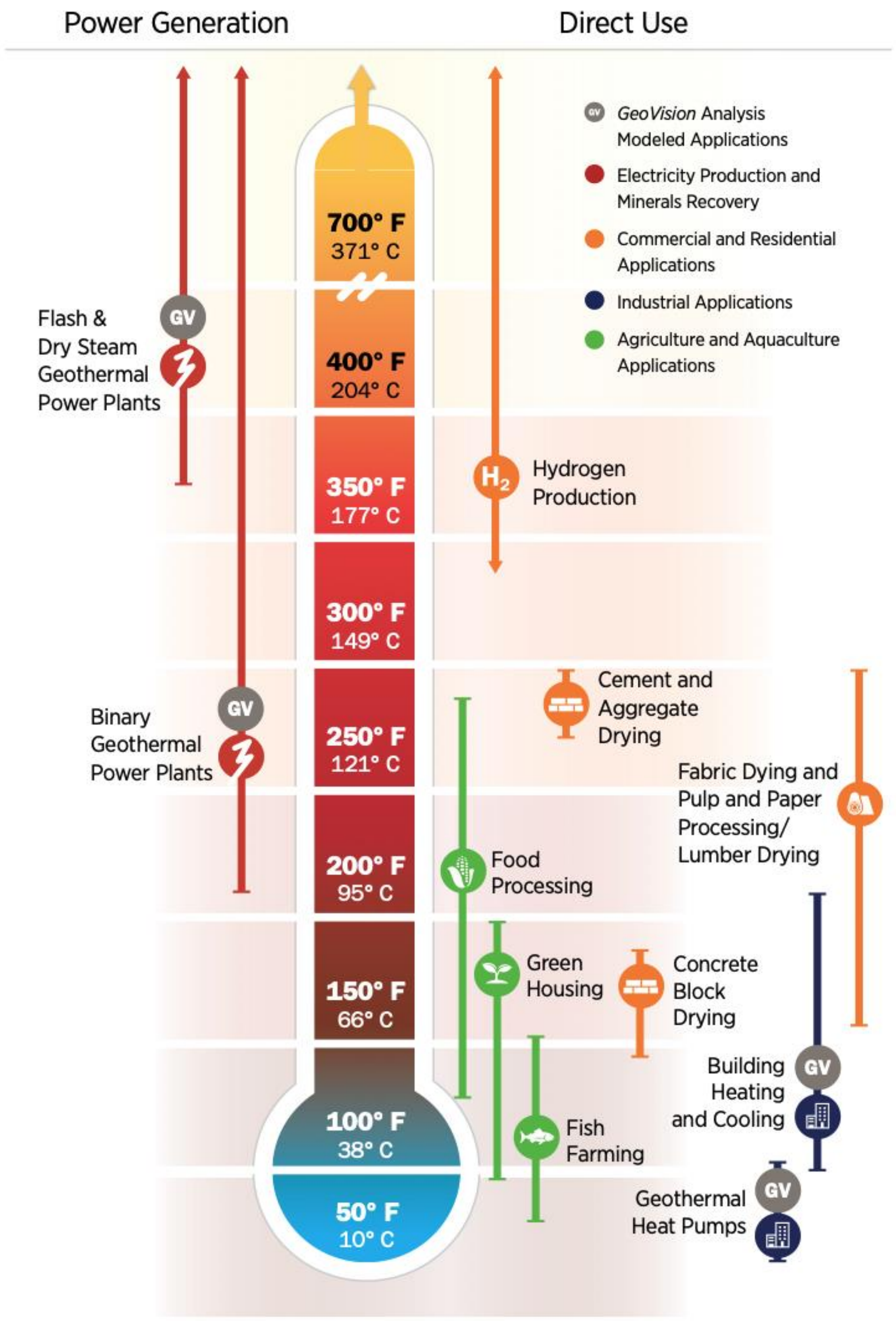
Geothermal energy mines heat to do work.

How do we move heat and convert it to work?

How do **fluids and materials** behave when heated and cooled?

How does this affect the energy balance of geothermal systems?

We need to understand the **thermodynamics** of geothermal systems.



Source: US Department of Energy, *U.S. GeoVision report, Chapter 2, p. 14*

Heat capacity

Heat capacity is a material property: different materials need different amounts of heat to achieve the same temperature difference.

Example: Consider two different material:

- When exposed to the same amount of heat, they will heat up to **two different temperatures**.
- When placed in contact, **heat flows spontaneously from the warmer material to the cooler material**.
- Eventually, both materials will be the **same temperature**, but **the amount of heat needed to bring each material to temperature is different**.

Conclusion:

Different materials will reach a state of equilibrium (i.e., a state in which no heat flows between them) only when they are the same temperature, but the amount of heat each material contains will be different.

Heat capacity

Reminder: Heat capacity is a measure of the heat that must be added to or removed from a material to change its temperature.

Changes in volume and pressure change heat capacity and we can define heat capacity in two ways:

- At constant volume (C_v)
- At constant pressure (C_p)

$$C = \frac{dQ}{dT}$$

The amount of heat that can be taken from a system to do work is equal to the number of degrees the temperature changes multiplied by the heat capacity:

$$C \times dT = dQ$$

Work and heat capacity

Reminder:

$$C \times dT = dQ$$

$\Delta E = Qv$ (constant volume, no work is done)

$\Delta H = H_2 - H_1 = [E_2 + (P \times V_2)] - [E_1 + (P \times V_1)] = Q_p$ (constant pressure, work is done)

Therefore:

$dH = C_p \times dT$, at constant pressure

$dE = C_v \times dT$, at constant volume

And:

$$dw = C_p \times dT$$

Gibbs function and Gibbs energy

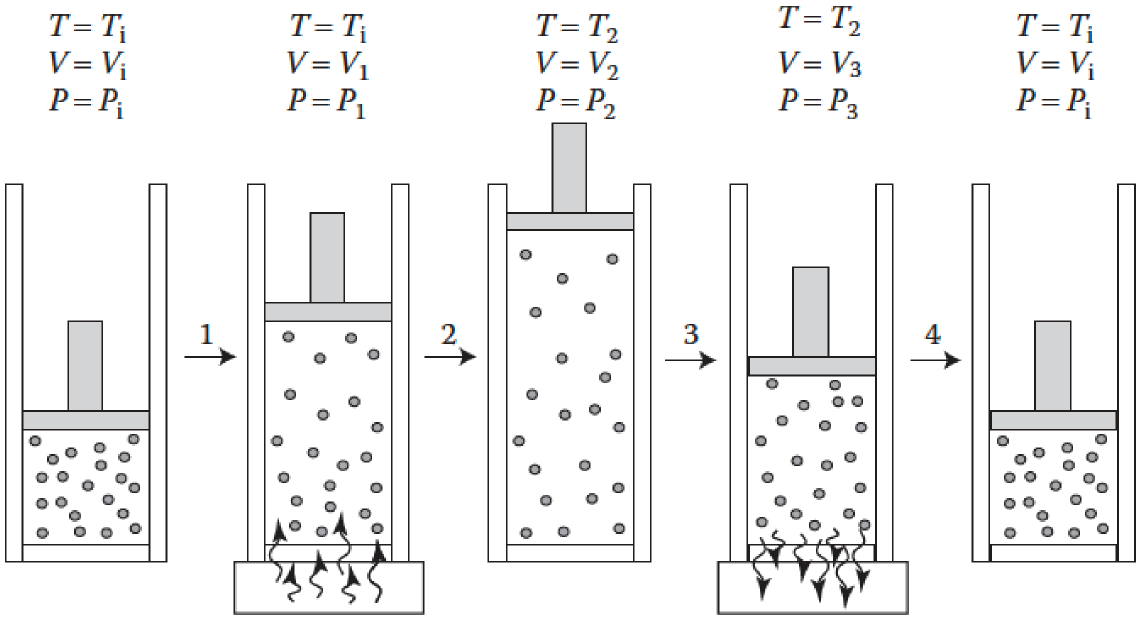
Total energy and the Carnot Cycle

In the Carnot cycle: we had no information about how we arrived at the initial state of the system.

A physical system does not record how it came to any given thermodynamic state.

We never know the absolute energy of a substance or system.

We can only determine how the internal energy **changes** as the system evolves from its current state to some other state.



Source: Glassley, W. E., *Geothermal Energy*

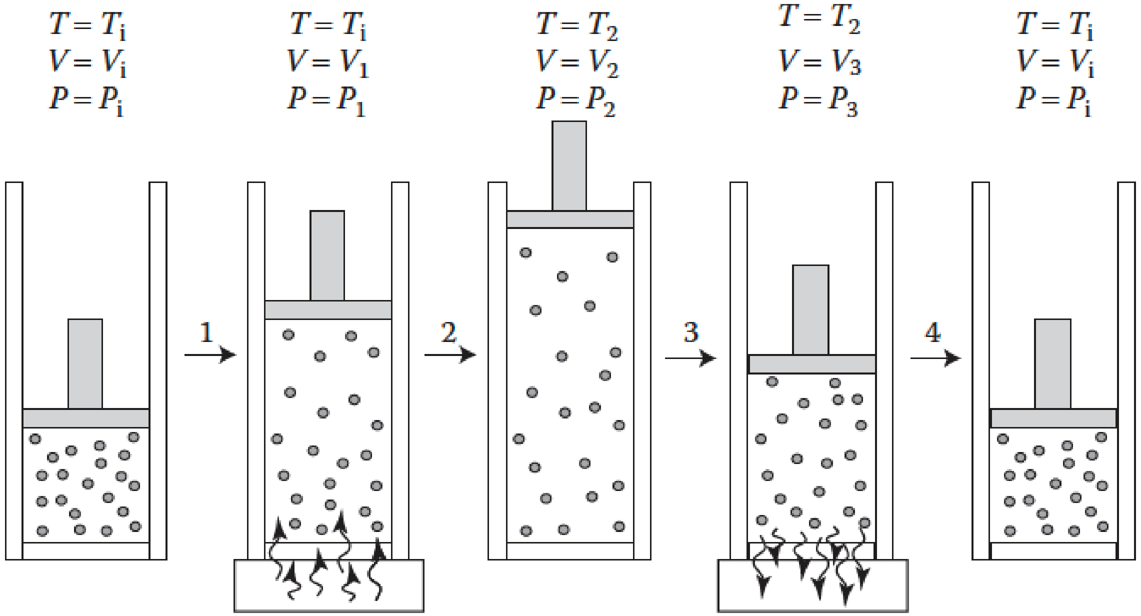
Total energy and the Carnot Cycle

We can **compare** two systems/substances and determine if they are in equilibrium and the absolute difference in their respective heat contents.

Key points:

Two systems at the same *T* cannot do work on each other.

Two systems at different *T* can do work on each other and are therefore a source of useful energy.



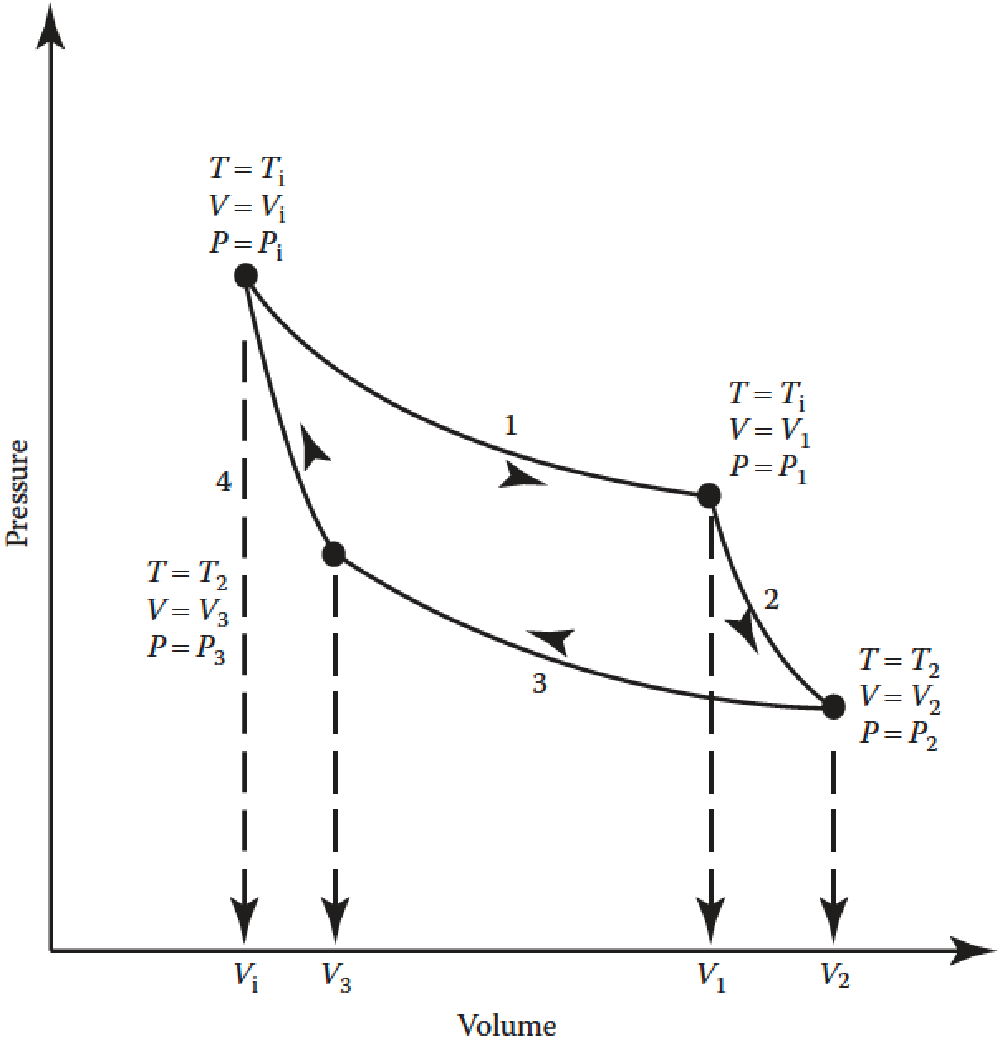
Source: Glassley, W. E., *Geothermal Energy*

How do we determine « useful work »?

We need to know the difference in the heat contents of the systems.

In the Carnot cycle, 3 fundamental attributes contribute to the energy of that system at any given point in the cycle:

1. the energy in the system at the initial set of conditions before the cycle begins
2. the energy of the system along an isothermal paths (the system gives up or gains energy)
3. the energy the system give up or gains during the adiabatic paths



Source: Glassley, W. E., *Geothermal Energy*

Gibbs function

Describes the energy in a system and how that energy is affected by changes in temperature and pressure.

The internal energy of a substance at some specified pressure (*P*) and temperature (*T*) is fully described through:

$$\Delta G_{P,T} = \Delta H_{P_1,T_1} - T \times \Delta S_{P_1,T_1} + \int_{T_1}^{T} \Delta C_p dT - T \times \int_{T_1}^{T} \frac{\Delta C_p}{T} dT + \int_{P_1}^{P} \Delta V dP$$

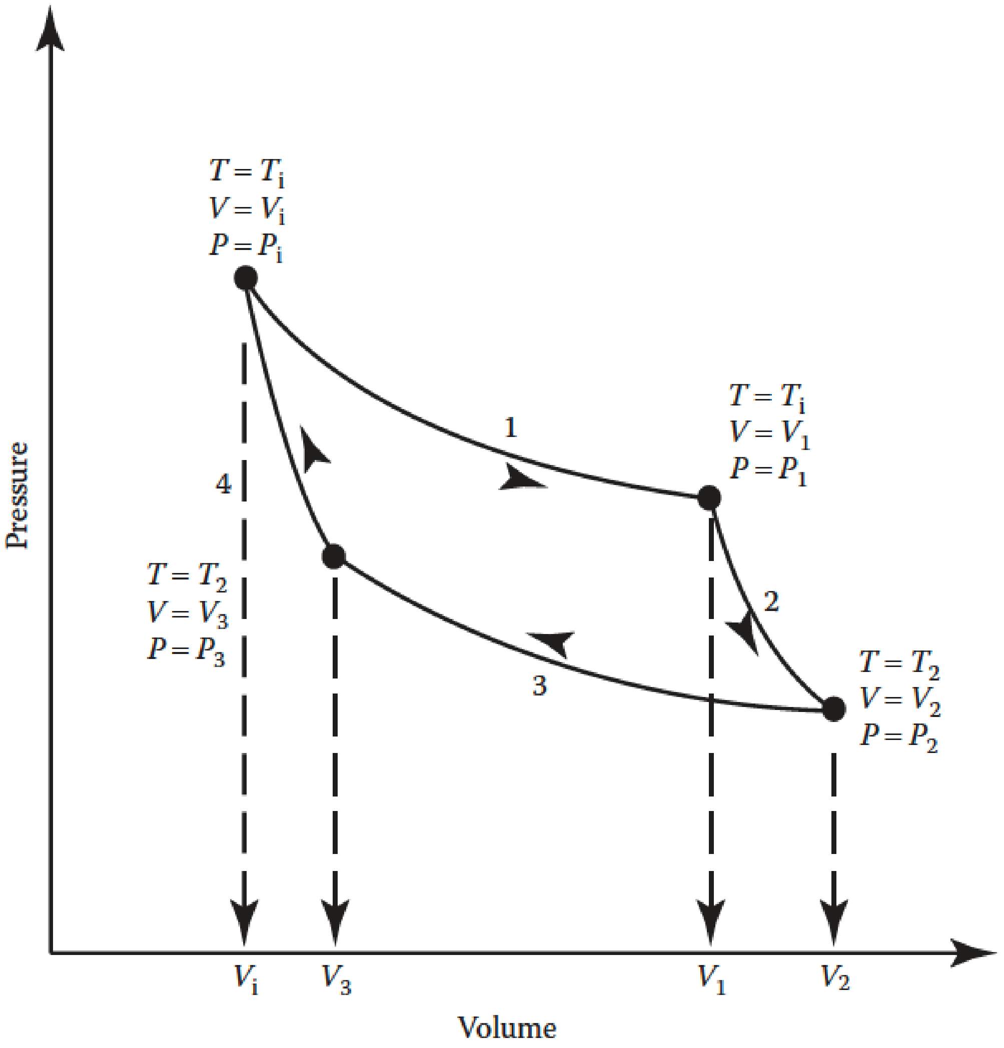
$\Delta G_{P,T}$ - Gibbs energy at *P* and *T*

$\Delta H_{P_1,T_1}$ - enthalpy at some standard state (generally 0.1 MPa, 298K)

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

ΔC_p - the heat capacity at constant pressure

ΔV - the change in volume



Source: Glassley, W. E., *Geothermal Energy*

Gibbs function and reference frames

We define the Gibbs energy of a substance with respect to some reference frame, which includes:

Reference materials: e.g., pure metal, pure elements, specific oxides, or compounds

Reference conditions: e.g., room temperature (298K) and pressure (0.1 MPa)

$$\Delta G_{P,T} = \Delta H_{P_1,T_1} - T \times \Delta S_{P_1,T_1} + \int_{T_1}^{T} \Delta C_p dT - T \times \int_{T_1}^{T} \frac{\Delta C_p}{T} dT + \int_{P_1}^{P} \Delta V dP$$

$\Delta G_{P,T}$ - Gibbs energy at *P* and *T*
$\Delta H_{P_1,T_1}$ - enthalpy at some standard state (generally 0.1 MPa, 298K)
$\Delta S_{P_1,T_1}$- entropy at the standard state
ΔC_p - the heat capacity at constant pressure
ΔV - the change in volume

Reference frames are established for convenience:

i.e., we define the energy content for the material at specified reference conditions (e.g., 0.0 *J*).

For geological applications, we usually go for: 298K (25°C, room *T*), 0.1 MPa (1 bar, room *P*).

Gibbs function and reference frames

Important:

The reference conditions and initial energy values determine the ***total*** internal energy values that are **computed** for a substance at any condition of interest.

But, the ***difference*** in internal energy from one set of conditions to another set of conditions will be exactly the same, regardless of reference frame.

The Gibbs function assumes reversible processes: it provides the ***maximum*** energy available in a system to do useful work.

$$\Delta G_{P,T} = \Delta H_{P_1,T_1} - T \times \Delta S_{P_1,T_1} + \int_{T_1}^{T} \Delta C_p dT - T \times \int_{T_1}^{T} \frac{\Delta C_p}{T} dT + \int_{P_1}^{P} \Delta V dP$$

$\Delta G_{P,T}$ - Gibbs energy at *P* and *T*
$\Delta H_{P_1,T_1}$ - enthalpy at some standard state (generally 0.1 MPa, 298K)
$\Delta S_{P_1,T_1}$- entropy at the standard state
ΔC_p - the heat capacity at constant pressure
ΔV - the change in volume

Standard state

The Gibbs function is cast in terms of Δ's of the thermodynamic properties.

This means we can compare states and properties ONLY on the basis of some **arbitrary reference system** that we define.

Usually, we assume that the Gibbs energy of formation of an element is 0 J at 0.1 MPa and 298K.

$$\Delta G_{P,T} = \Delta H_{P_1,T_1} - T \times \Delta S_{P_1,T_1} + \int_{T_1}^{T} \Delta C_p dT - T \times \int_{T_1}^{T} \frac{\Delta C_p}{T} dT + \int_{P_1}^{P} \Delta V dP$$

$\Delta G_{P,T}$ - Gibbs energy at *P* and *T*
$\Delta H_{P_1,T_1}$ - enthalpy at some standard state (generally 0.1 MPa, 298K)
$\Delta S_{P_1,T_1}$- entropy at the standard state
ΔC_p - the heat capacity at constant pressure
ΔV - the change in volume

Standard state

Example: $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

Assume this reaction takes place at standard conditions in a calorimeter.

(Calorimeter: instrument that measures the heat given off or absorbed by a reaction.)

The heat given off by the formation of a water molecule would be the energy of formation of water at a standard *T* and *P.*

We can do this with all simple oxides and compounds.

The resulting data + Gibbs function allow us to determine the thermodynamic properties of all minerals and fluids.

$$\Delta G_{P,T} = \Delta H_{P_1,T_1} - T \times \Delta S_{P_1,T_1} + \int_{T_1}^{T} \Delta C_p dT - T \times \int_{T_1}^{T} \frac{\Delta C_p}{T} dT + \int_{P_1}^{P} \Delta V dP$$

$\Delta G_{P,T}$ - Gibbs energy at *P* and *T*
$\Delta H_{P_1,T_1}$ - enthalpy at some standard state (generally 0.1 MPa, 298K)
$\Delta S_{P_1,T_1}$- entropy at the standard state
ΔC_p - the heat capacity at constant pressure
ΔV - the change in volume

Equations of state

Example: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

Let's redo the calorimetric measurements at different *P* and *T*.

We can develop equations of state which define how the energy content of a material changes with *P* and *T*.

These equations of state help us to determine the energy content of our systems at any set of conditions of interest.

$$\Delta G_{P,T} = \Delta H_{P_1,T_1} - T \times \Delta S_{P_1,T_1} + \int_{T_1}^{T} \Delta C_p dT - T \times \int_{T_1}^{T} \frac{\Delta C_p}{T} dT + \int_{P_1}^{P} \Delta V dP$$

$\Delta G_{P,T}$ - Gibbs energy at *P* and *T*

$\Delta H_{P_1,T_1}$ - enthalpy at some standard state (generally 0.1 MPa, 298K)

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

ΔC_p - the heat capacity at constant pressure

ΔV - the change in volume

Equations of state: Energy content of water at *P* and *T*

Heat water at constant pressure.

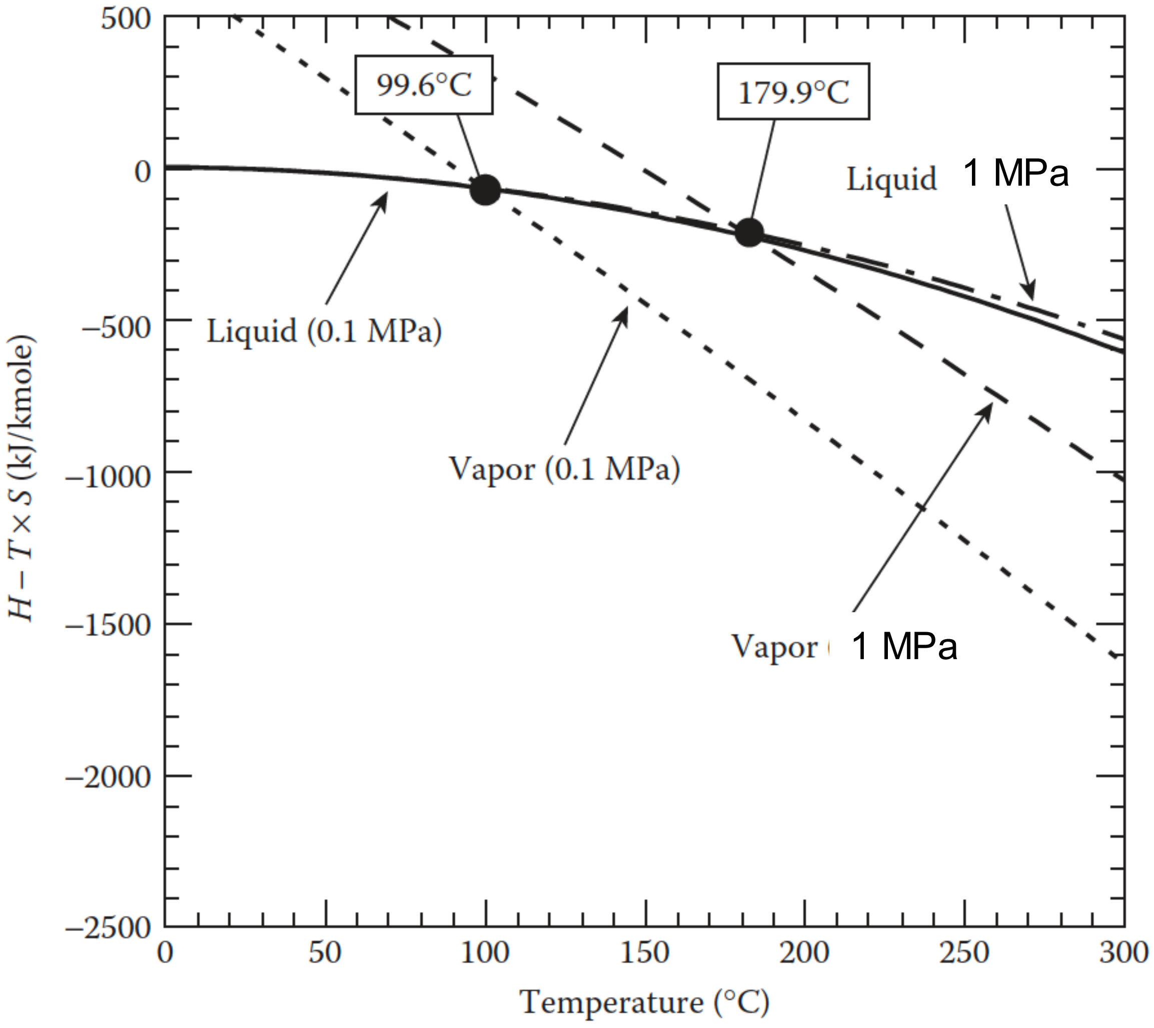
The change in Gibbs energy is equivalent to the enthalpy contributed by the heating process minus the product of the temperature times the entropy change:

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

Equations of state: Energy content of water at *P* and *T*

What is the effect of temperature on the Gibbs' energy of liquid and vapour?

What is the effect of pressure on the Gibbs' energy of liquid and vapour?



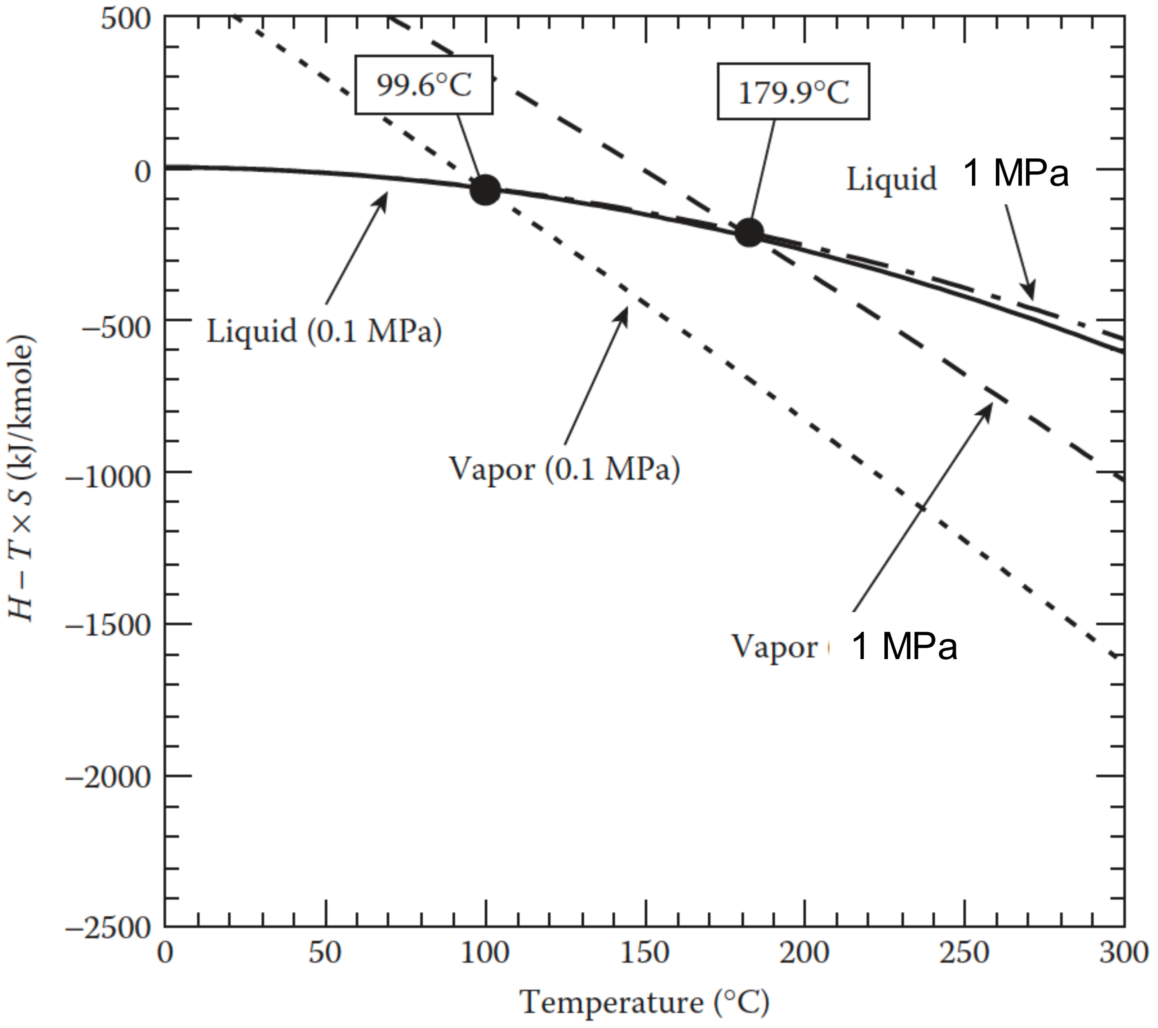
Source: Glassley, W. E., *Geothermal Energy*

Equations of state: energy content of water at *P* and *T*

1. At contant *P* changes in T affect a vapour phase more severely than a liquid
2. At modest *P*, pressure has minimal effect on changes in the thermodynamic properties of liquids (and solids), but can dramatically change the properties of gases

Points 1 and 2 imply that the energy content of gases is sensitive to physical conditions they experience: **key for geothermal energy**.

Why does water change phase from liquid to vapour?



Source: Glassley, W. E., *Geothermal Energy*

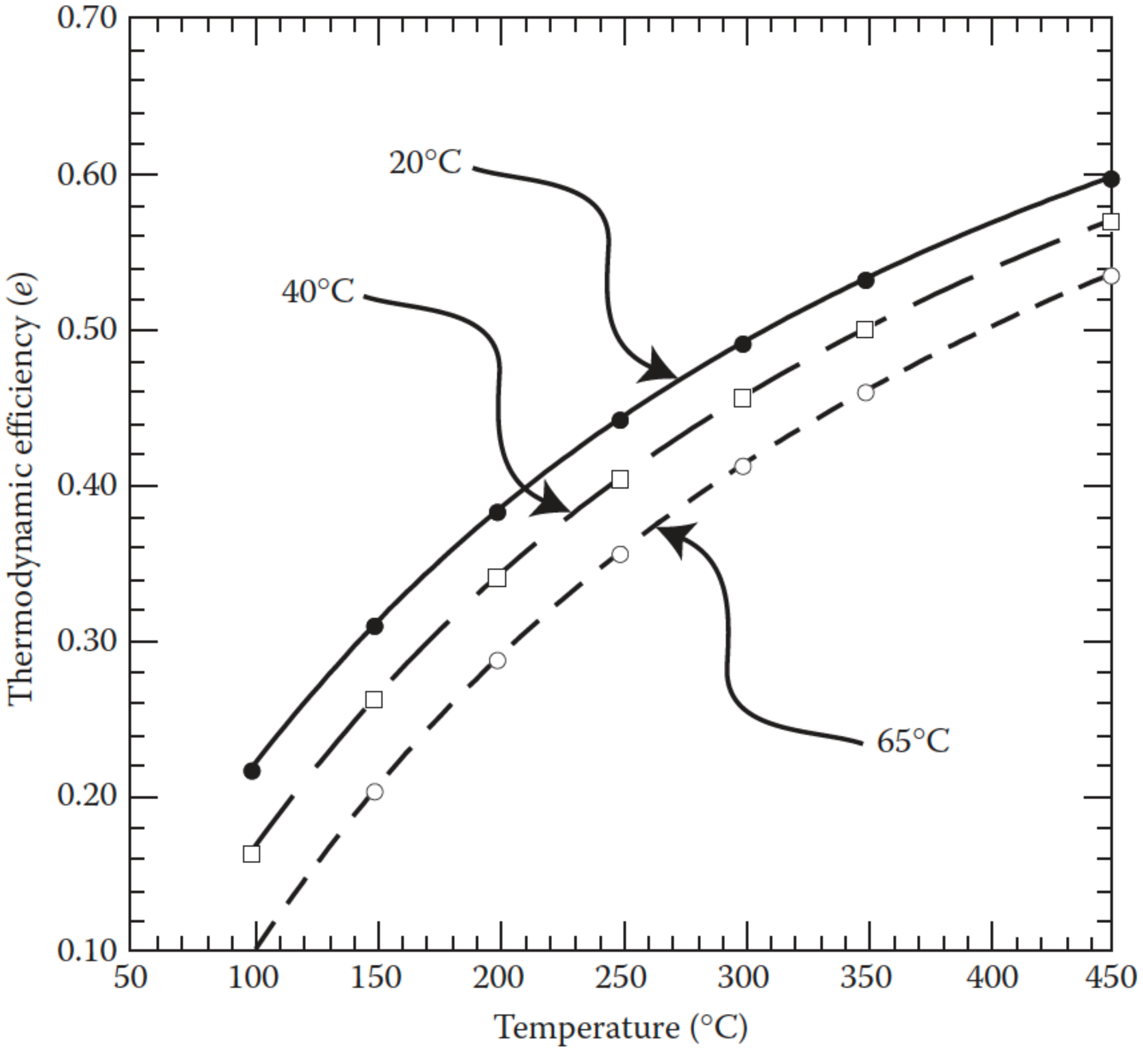
Thermodynamic efficiency

Thermodynamic efficiency

$e = -\frac{w}{Q} = \frac{\Delta Q}{Q_{in}}$, depends only on temperature

Steps 2 and 4 of the Carnot engine are adiabatic: no heat is added or removed from the system: $e = \frac{\Delta Q}{Q_{in}} = \frac{(T_i - T_2)}{T_i}$, T_i is the initial T and T_2 is the temperature of the cooled gas.

This is thermodynamic efficiency.



Source: Glassley, W. E., *Geothermal Energy*

Thermodynamic efficiency

$e = -\frac{w}{Q} = \frac{\Delta Q}{Q_{in}}$, depends on temperature.

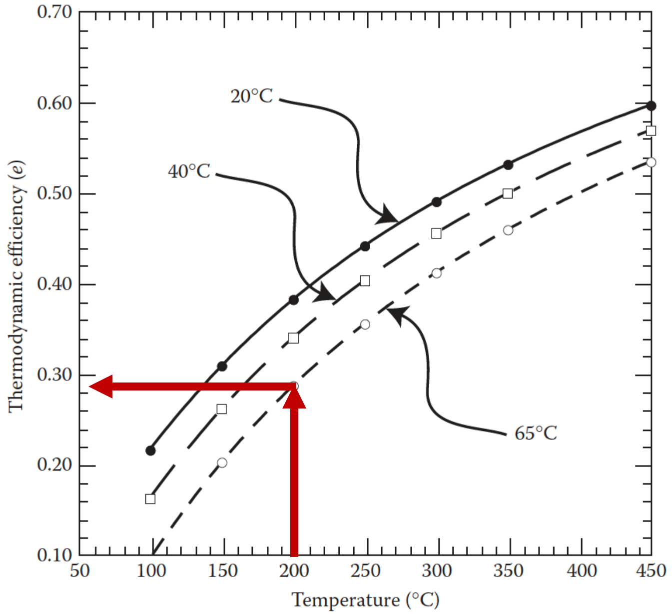
It's important to achieve the **greatest *T* difference** possible between a working fluid and its cooled state in any cyclic process.

Geothermal reservoirs: 5% to 10% absolute increase in effiiency for every 50°C increase in working fluid temperature.

Things to keep in mind:

In nature, thermodynamic efficiency depends on the depth of extraction because the fluid experiences a pressure change.

The thermodynamic properties of water are very important.



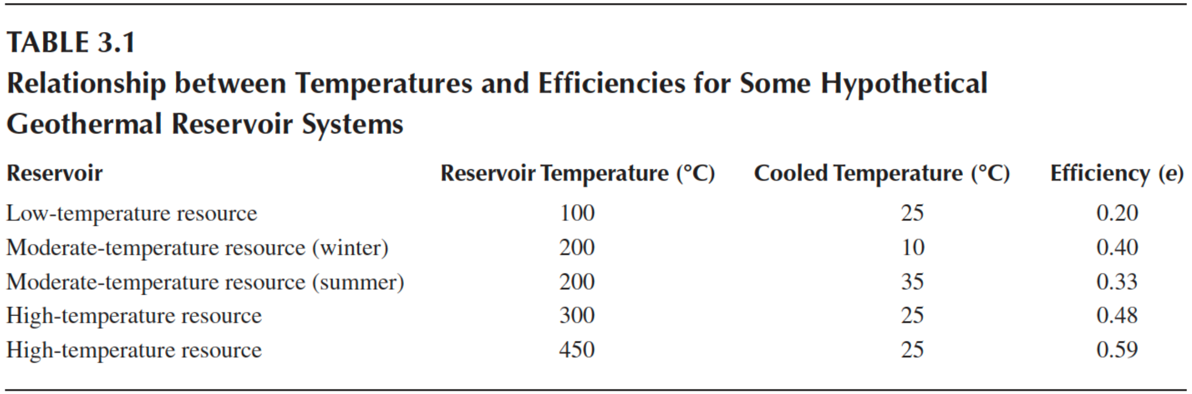


TABLE 3.1
Relationship between Temperatures and Efficiencies for Some Hypothetical Geothermal Reservoir Systems

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

Source: Glassley, W. E., *Geothermal Energy*

Key points

1. Heat and work are directly related
2. The maximum amount of heat that can be converted to work is independent of pathway
3. All substances possess some quantity of heat
4. Gibbs function: Defines the available heat by considering the attributes and state of the system
5. To calculate Gibbs energy you need: enthalpy, entropy, heat capacity, T, P
6. Systems exist in their lowest-energy state
7. The availability of heat to do work depends on the temperature difference between the substance and its surroundings

Case Study: Thermodynamic properties of water

Each phase has characteristic molar enthalpy, volume, heat capactiy, and entropy.

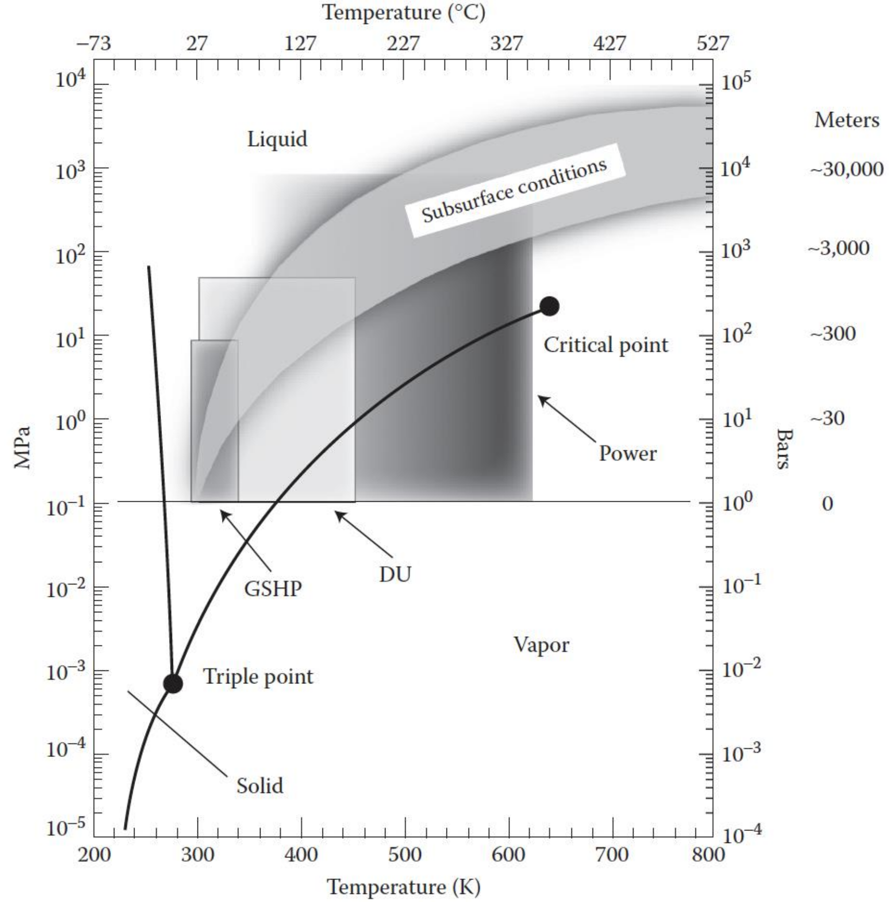


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

Example: Heat capacity

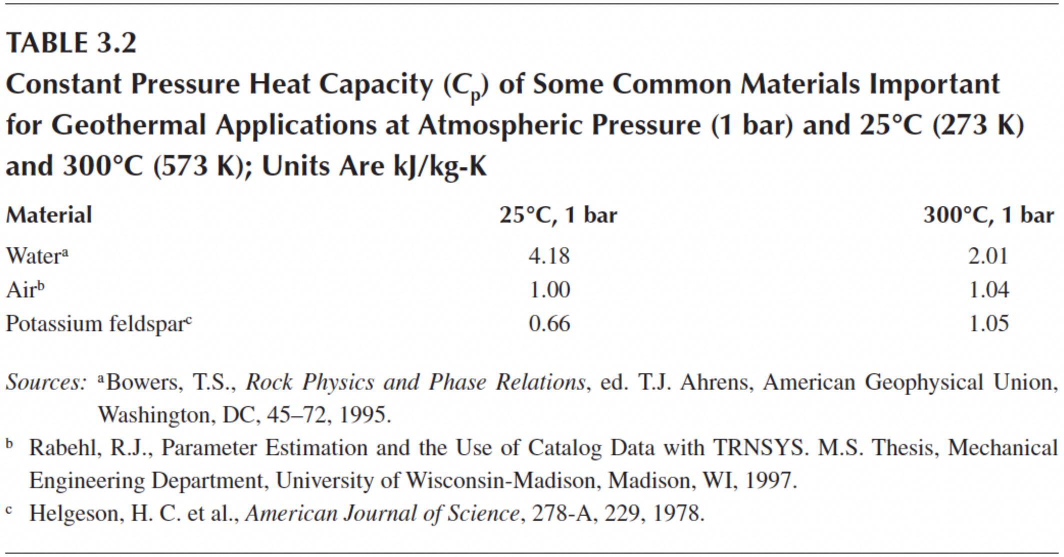


TABLE 3.2

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: [a] Bowers, 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.

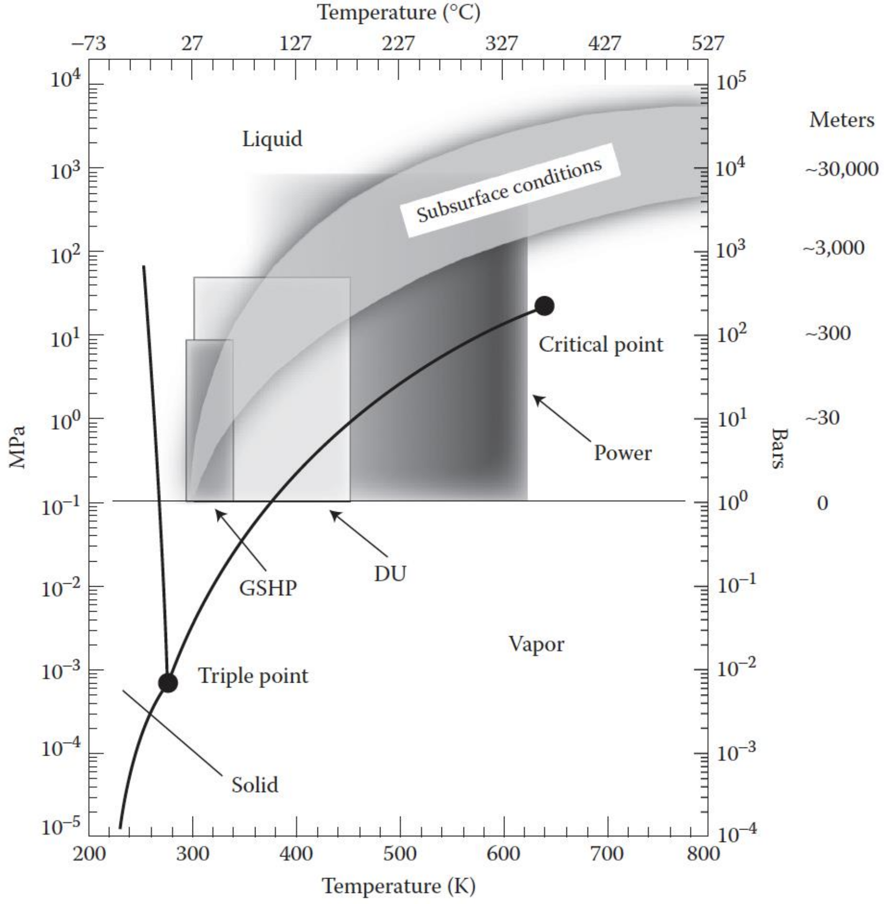


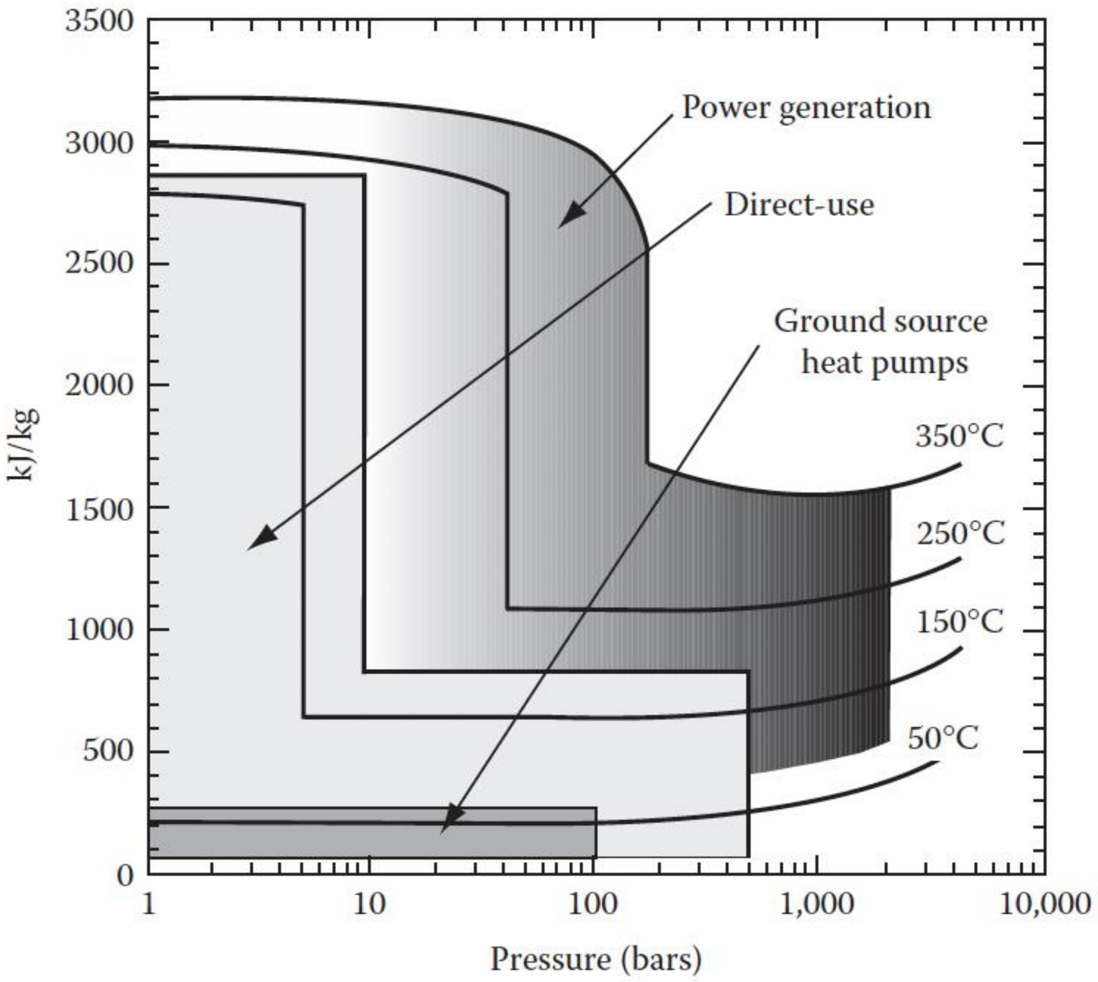
FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

Enthalpy vs. pressure for water.

What is the approximate enthalpy of water in the liquid state at near-surface conditions (P < 100 bars, T < 50°C)?



Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

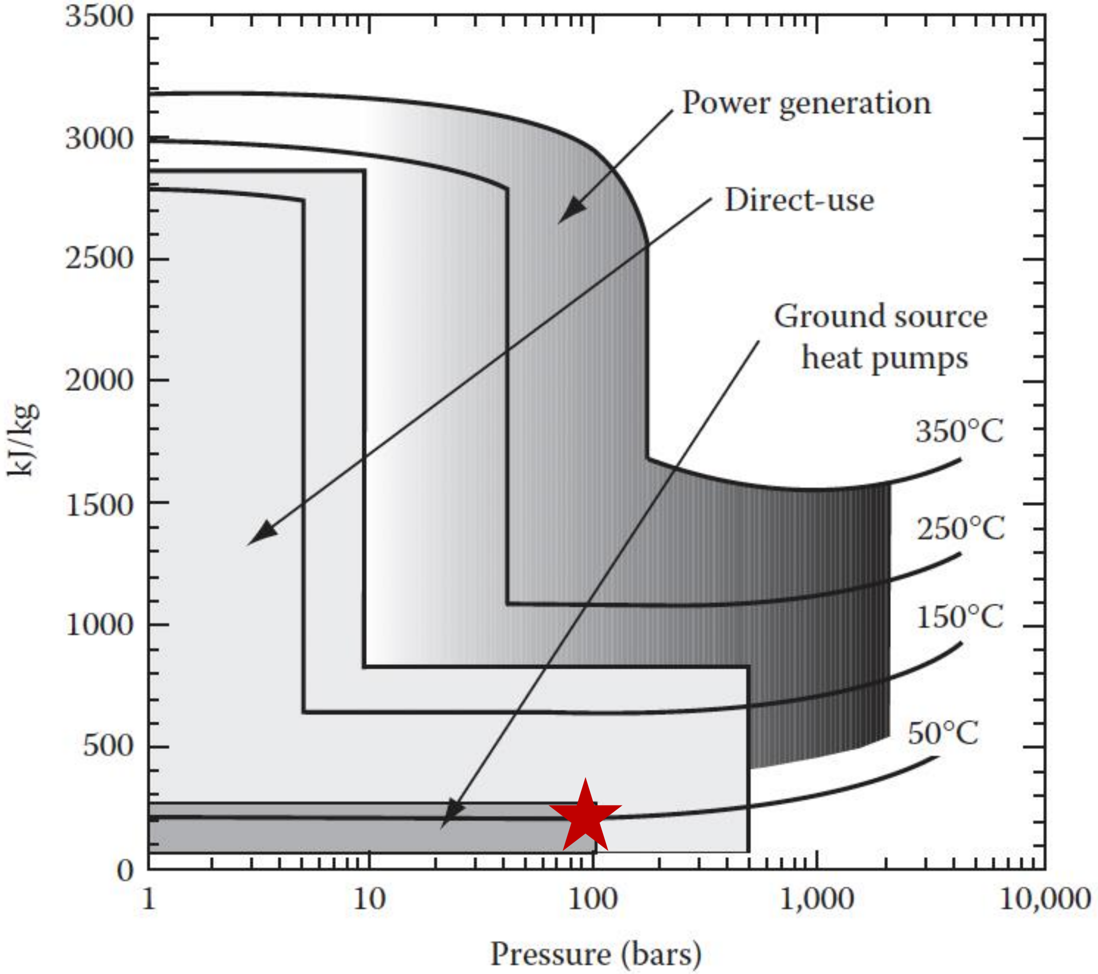
Enthalpy vs. pressure for water.

What is the approximate enthalpy of water in the liquid state at near-surface conditoins (P < 100 bars, T < 50°C)?

About 200 kJ/kg

We will set this as a reference internal energy that the water contains.

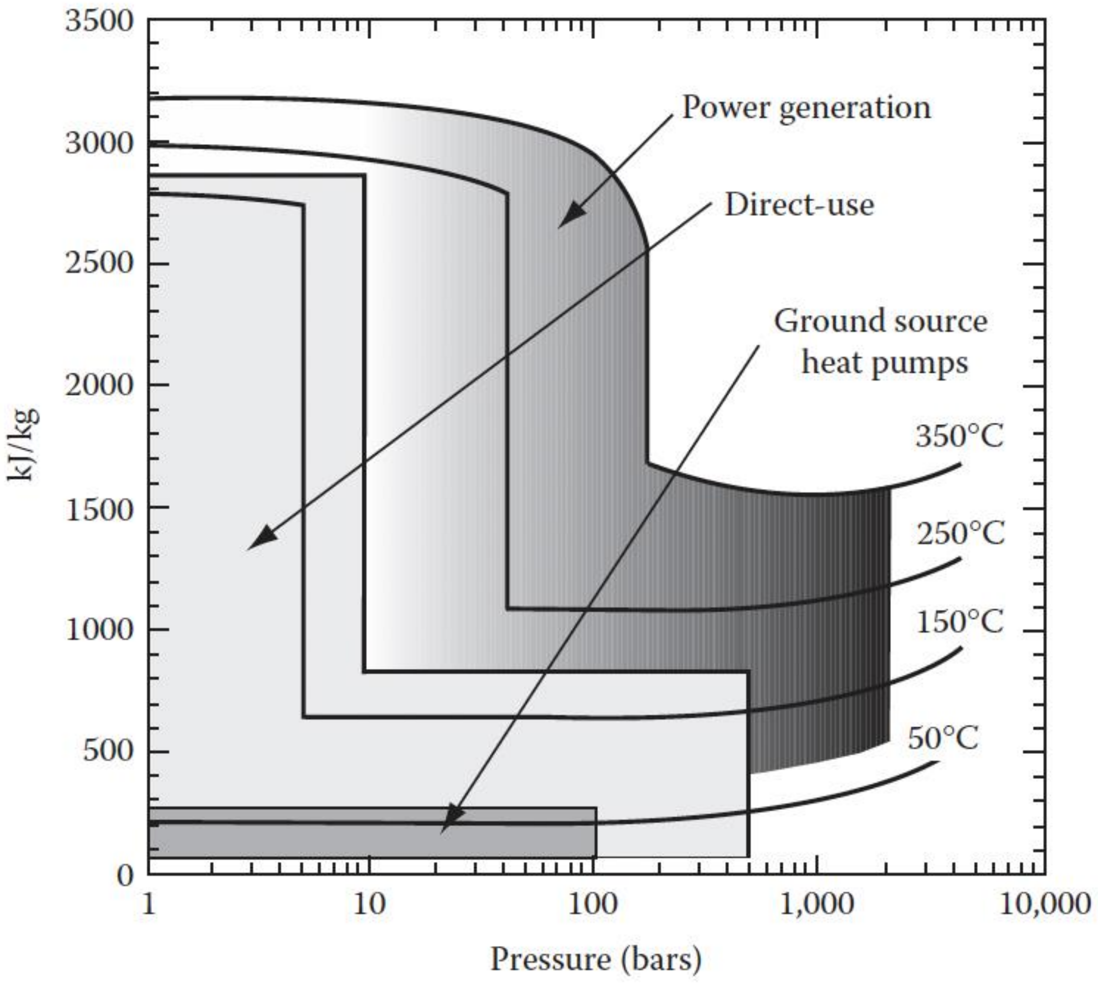
(Hint: 1 kg of water at these conditions has a volume of approximately 1 L.)



Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

If you have a ground source heat pump that removes 1000 J of heat energy from 1 L of water, by what percent do you change the enthalpy of that volume of water?

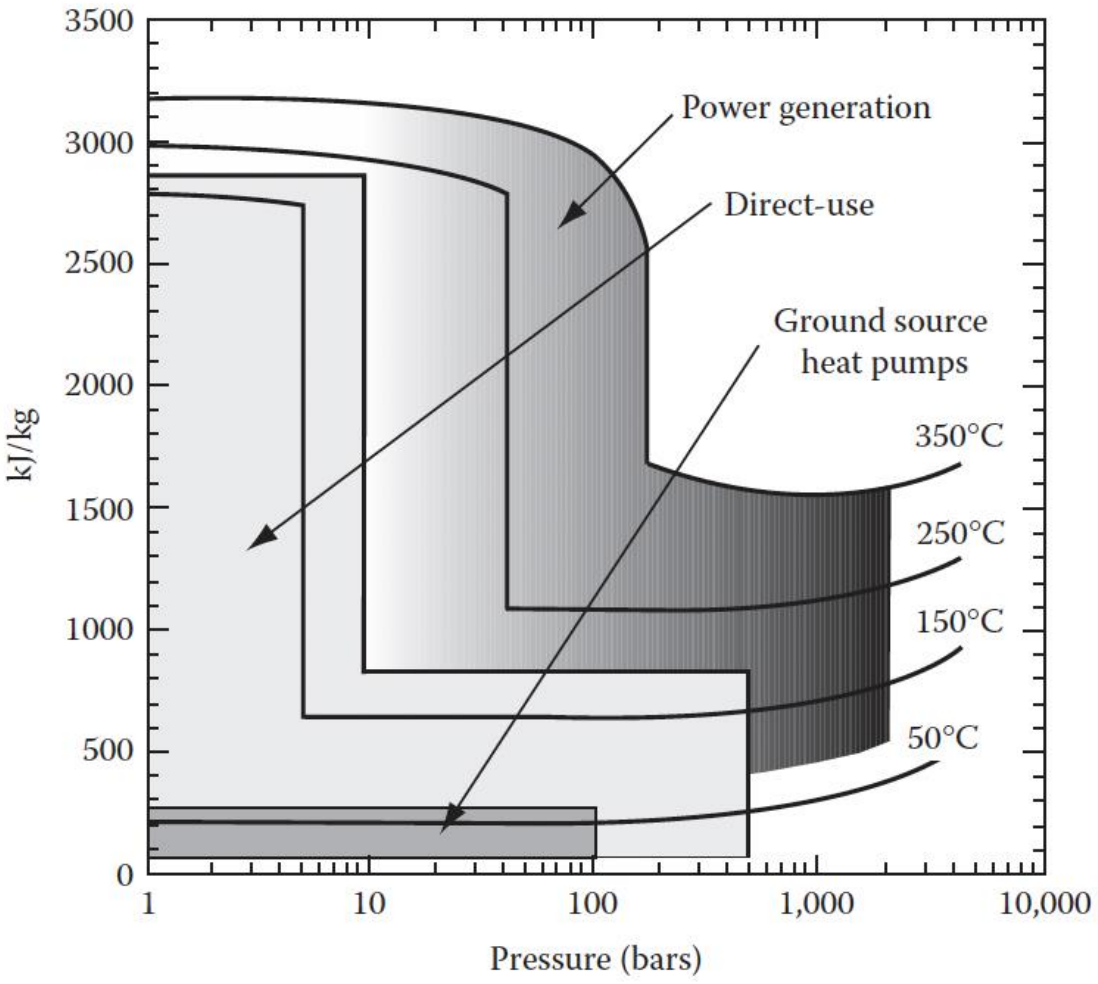


Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

If you have a ground source heat pump that removes 1000 J of heat energy from 1 L of water, by what percent do you change the enthalpy of that volume of water?

By how much does the temperature of this volume of water change?



Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What happens across a phase change?

Consider a water-saturated geothermal reservoir at a depth of 1500 m and 250°C.

We will assume that pumping the water to the surface is an **adiabatic process**.

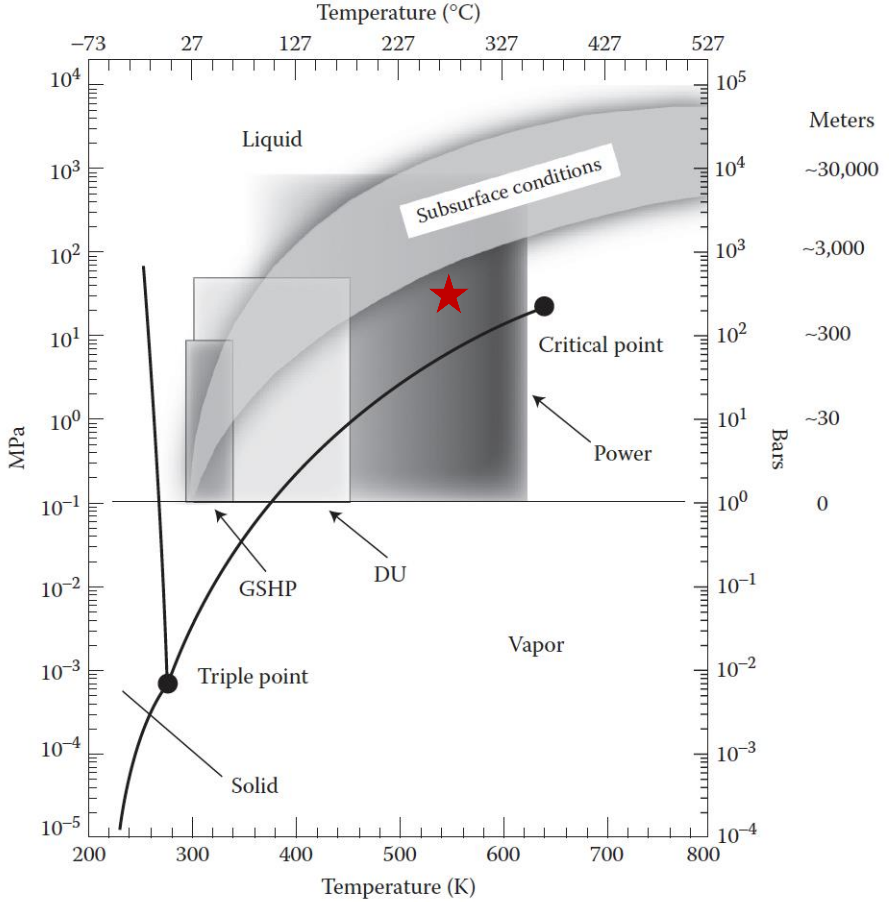


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What happens across a phase change?

Consider a water-saturated geothermal reservoir at a depth of 1500 m and 250°C.

We will assume that pumping the water to the surface is an **adiabatic process**.

This process is irreversible:

Constant enthalpy

Entropy changes.

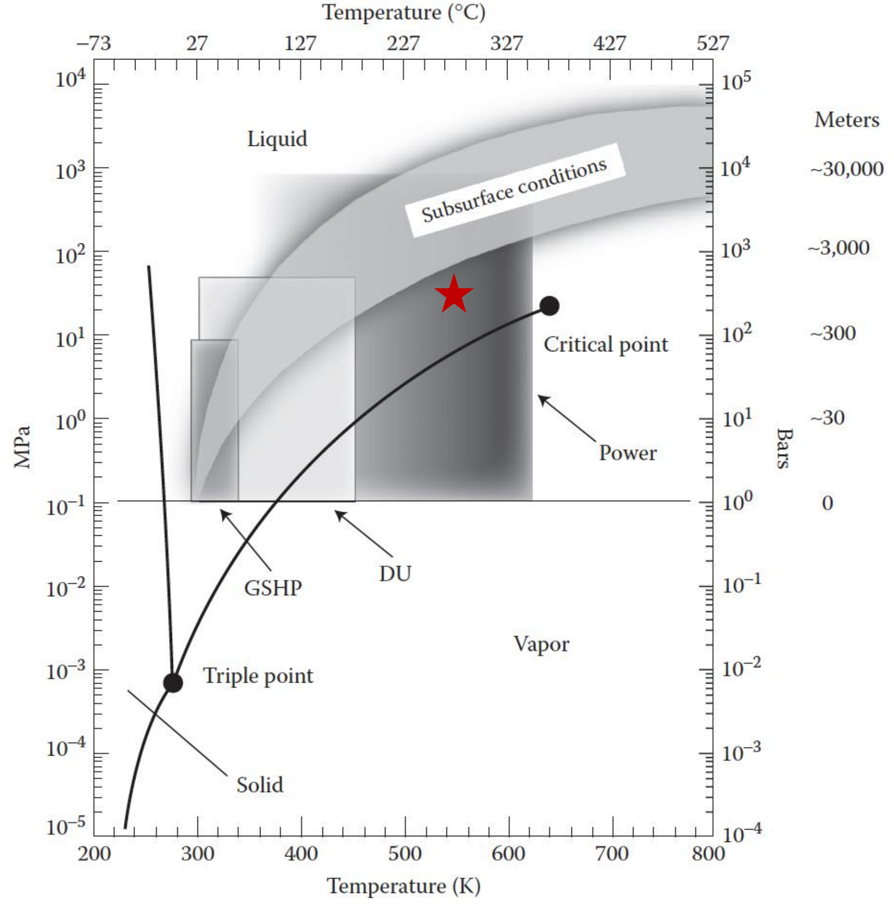


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What happens across a phase change?

Consider a water-saturated geothermal reservoir at a depth of 1500 m and 250°C.

As the water ascends, pressure drops.

Water crosses the liquid-vapour boundary at about 40 bars (assuming 250°C).

At this point, vapour begins to separate from liquid, as bubbles: **Flashing**

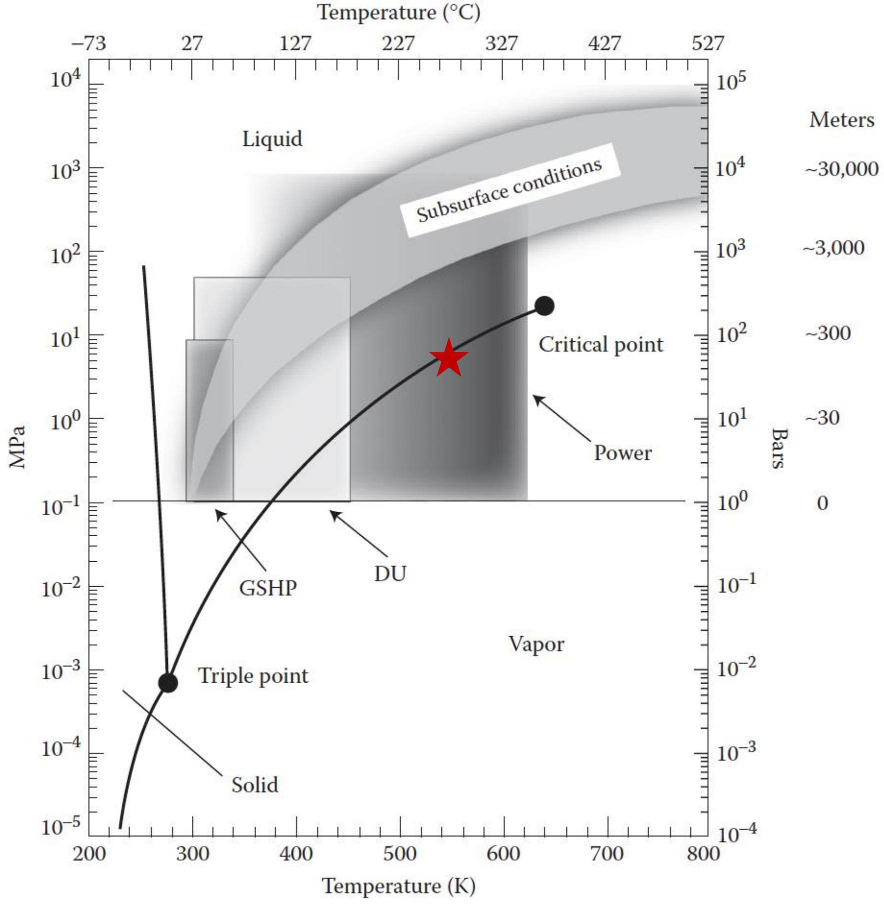


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What happens across a phase change?

As water continues to ascend, temperature will follow the phase boundary.

Why?

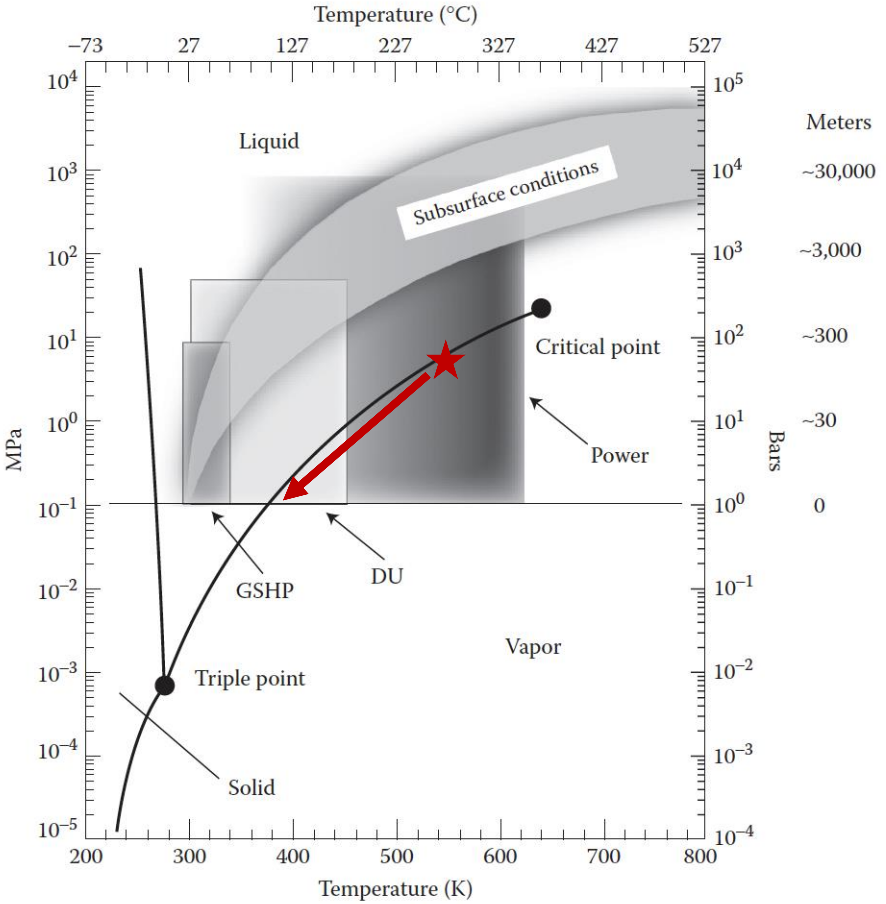


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What happens across a phase change?

Assume:

The water leaves the wellhead at 100°C.

No heat or mass leaves the system.

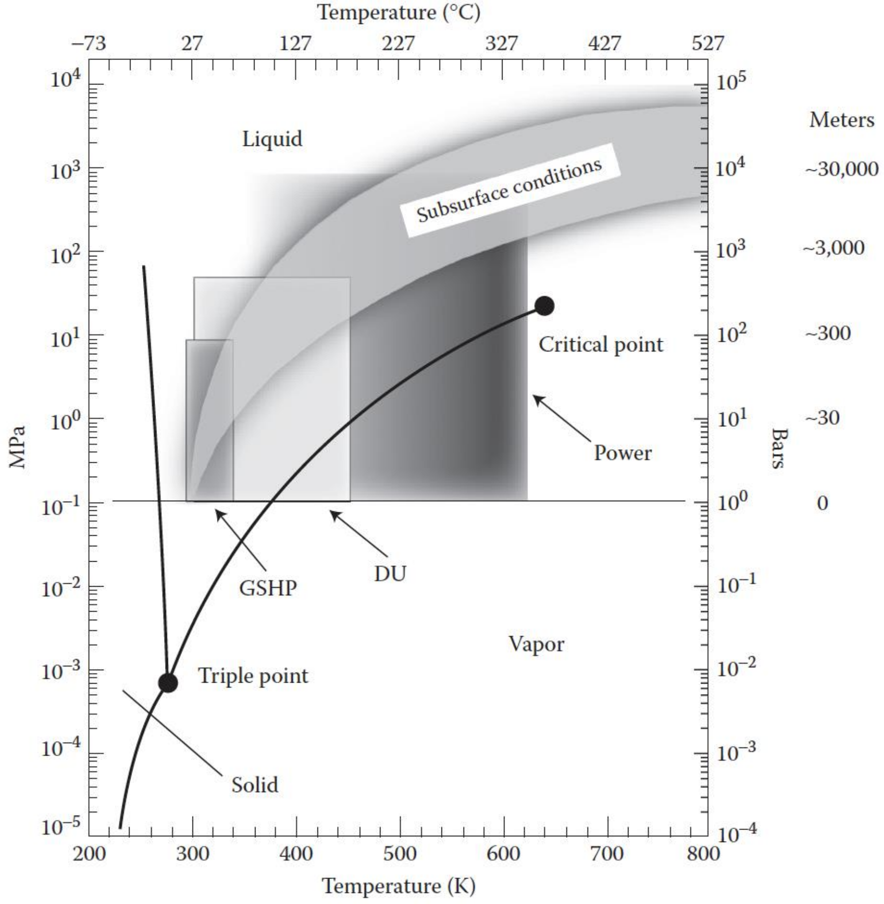


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What happens across a phase change?

Assume:

The water leaves the wellhead at 100°C.

No heat or mass leaves the system.

This means:

Combined (liquid+vapour) enthalpy is constant.

Combined (liquid+vapour) mass is constant.

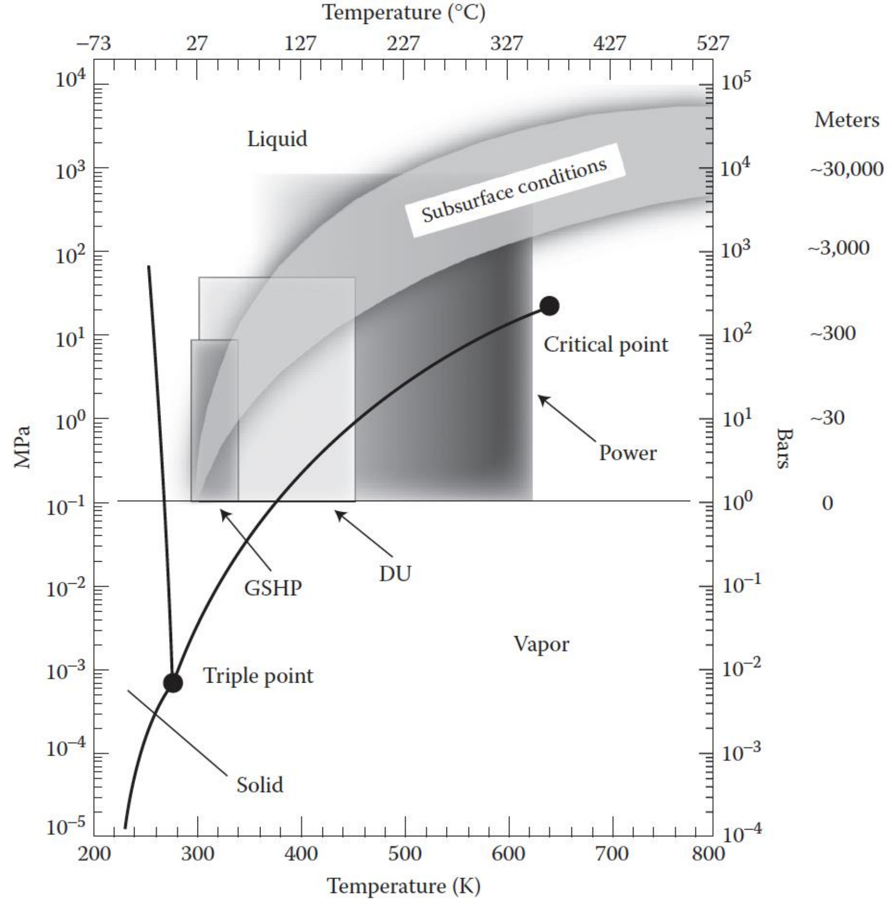


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

Heat and mass balance

Because the system has constant enthalpy:

$$H_{l,250°C} = x \times H_{l,100°C} + (1-x) \times H_{v,100°C}$$

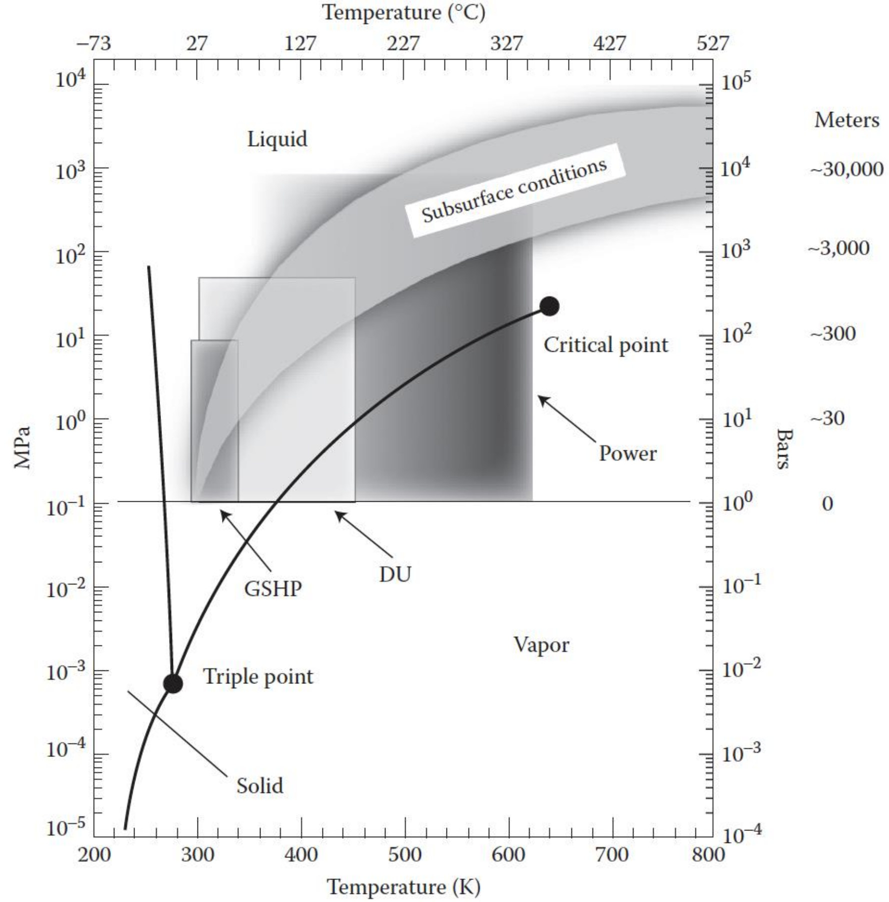


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

Heat and mass balance

Because the system has constant enthalpy:

$$\boxed{H_{l,250°C}} = \boxed{x \times H_{l,100°C} + (1-x) \times H_{v,100°C}}$$

Enthalpy at beginning of extraction

Enthalpy at end of extraction

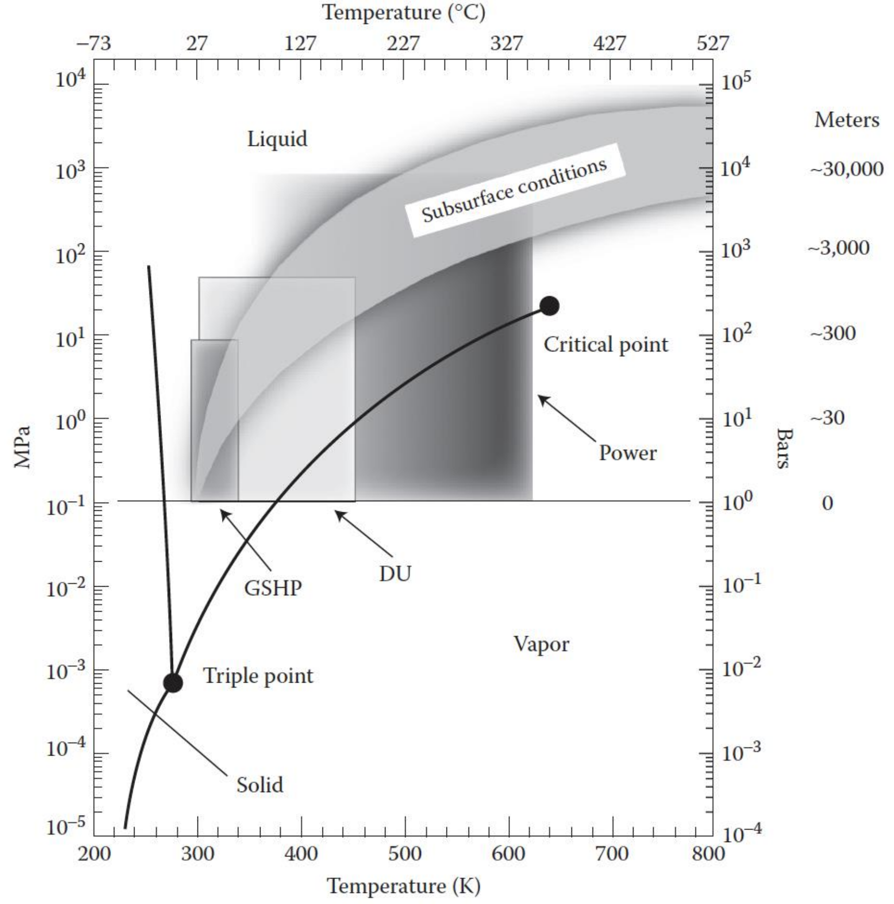


FIGURE 3.7 Phase diagram for water. Temperatures are indicated in degrees Celsius (upper horizontal axis) and Kelvin (lower horizontal axis), and pressures are indicated in megapascals (left vertical axis) and bars (right vertical axis). Also indicated on the right of the figure is the approximate equivalent 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).

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

What is the enthalpy of the reservoir if:

Conditions at the bottom of a 3 km well:

1000 bar

Conditions at the top of the well:

100°C, 1 bar, fluid is 70% liquid and 30% vapour.

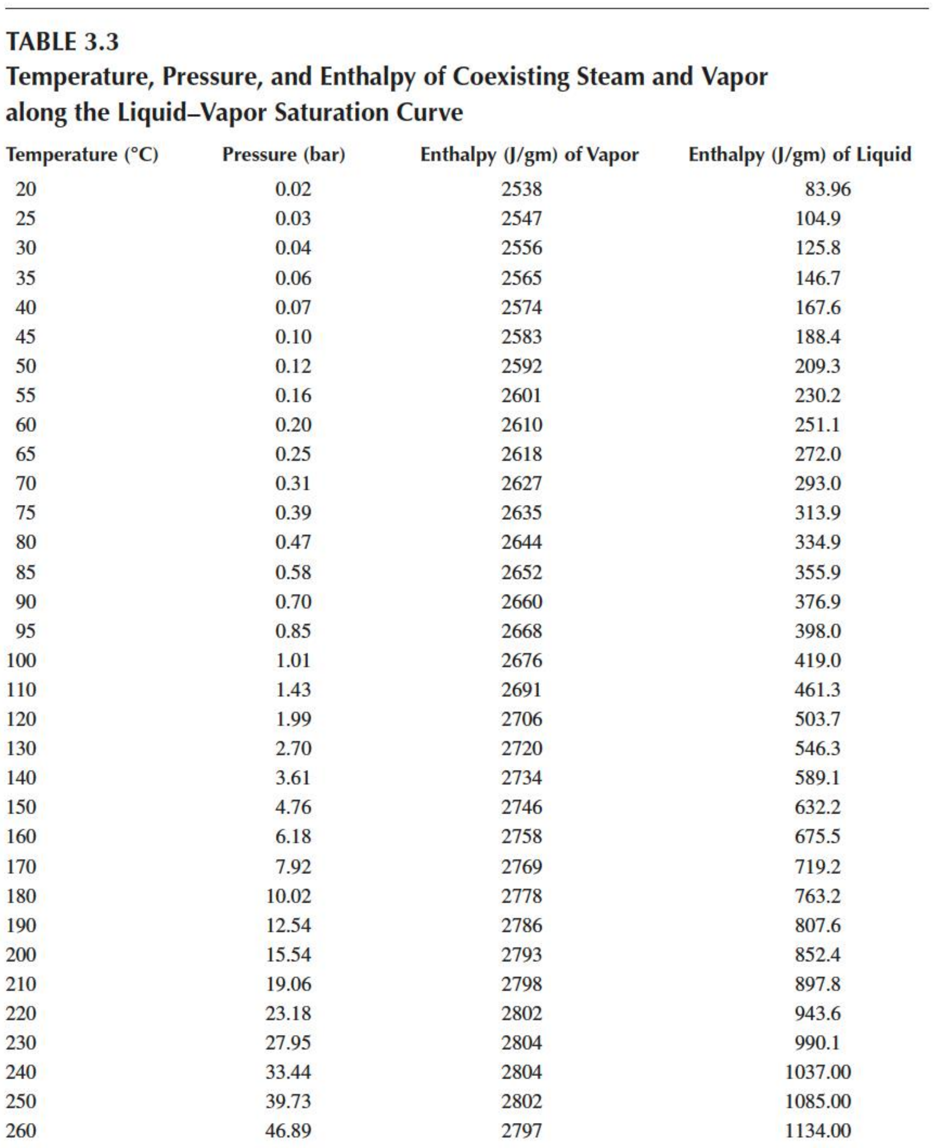


TABLE 3.3

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

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

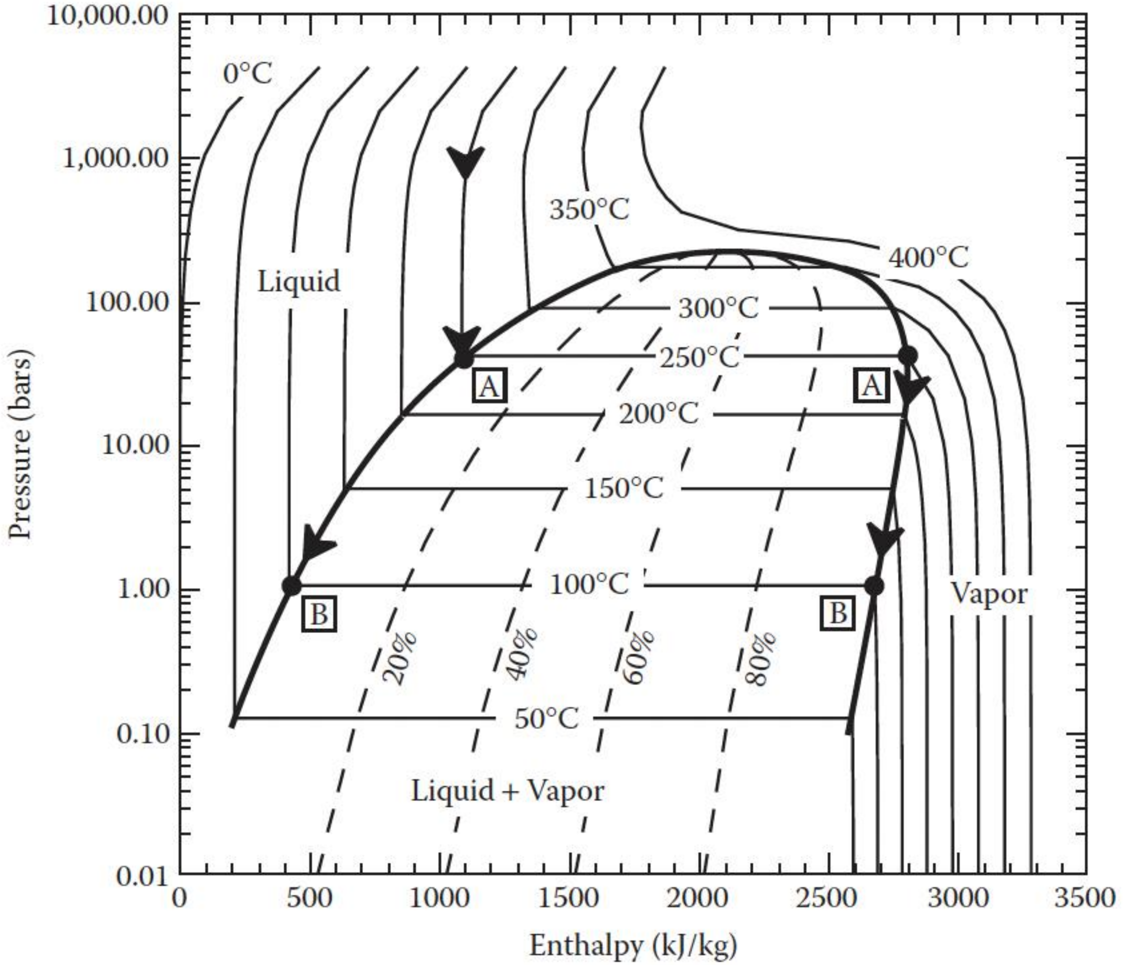


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure–enthalpy path followed by a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

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

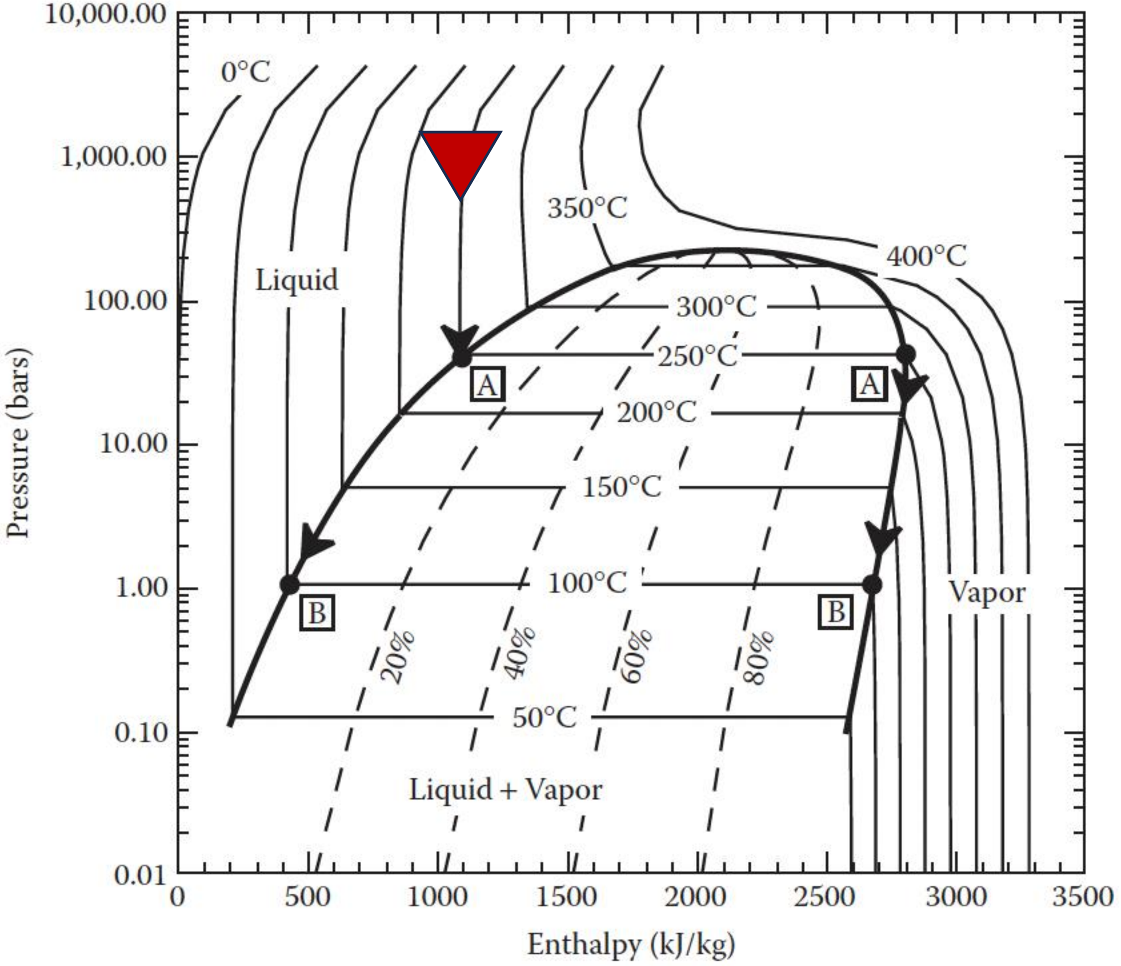


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure–enthalpy path followed by a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

Start: 250°C and 1000 bars.

H_l = 1113 J/gm

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

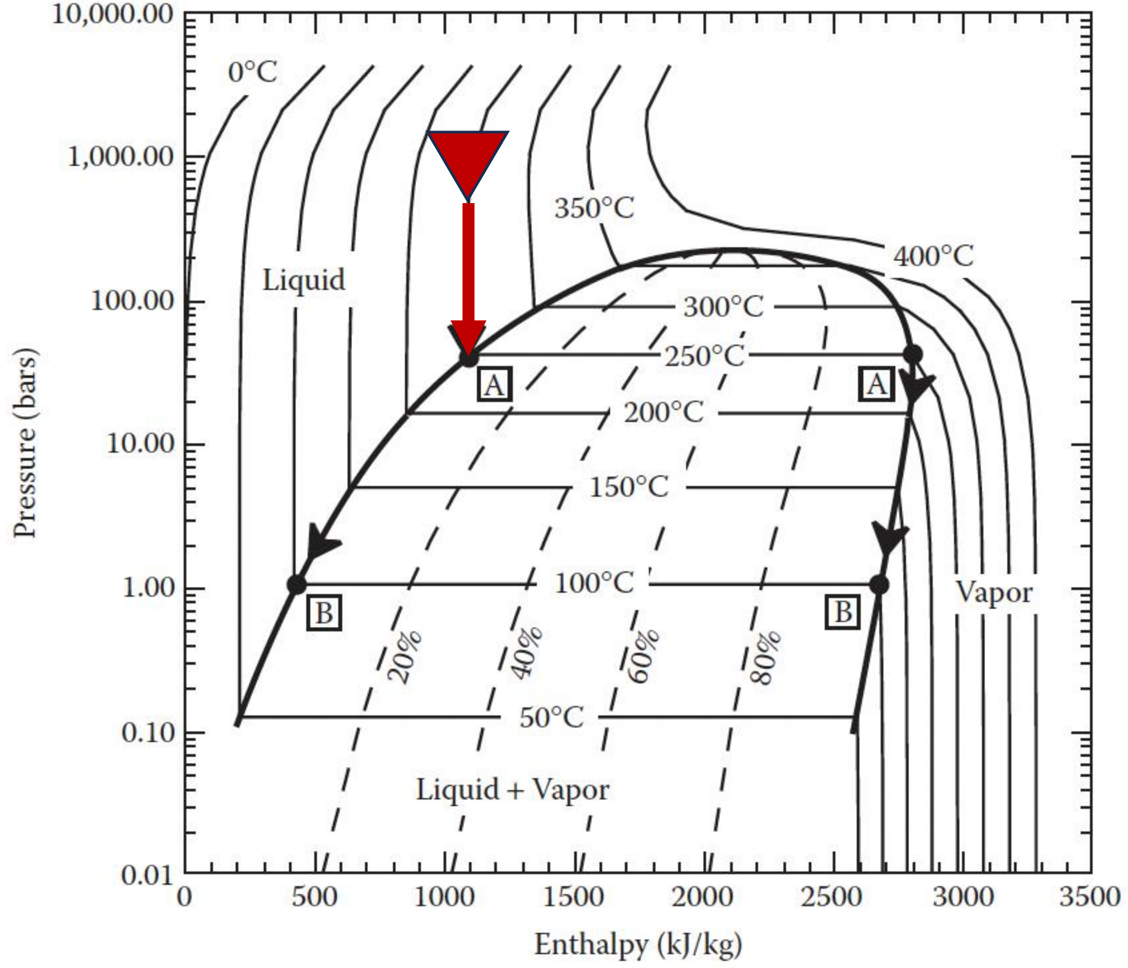


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure–enthalpy path followed by a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

Start: 250°C and 1000 bars.

H_l = 1113 J/gm

Fluid ascends to 40 bar.

What happens?

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

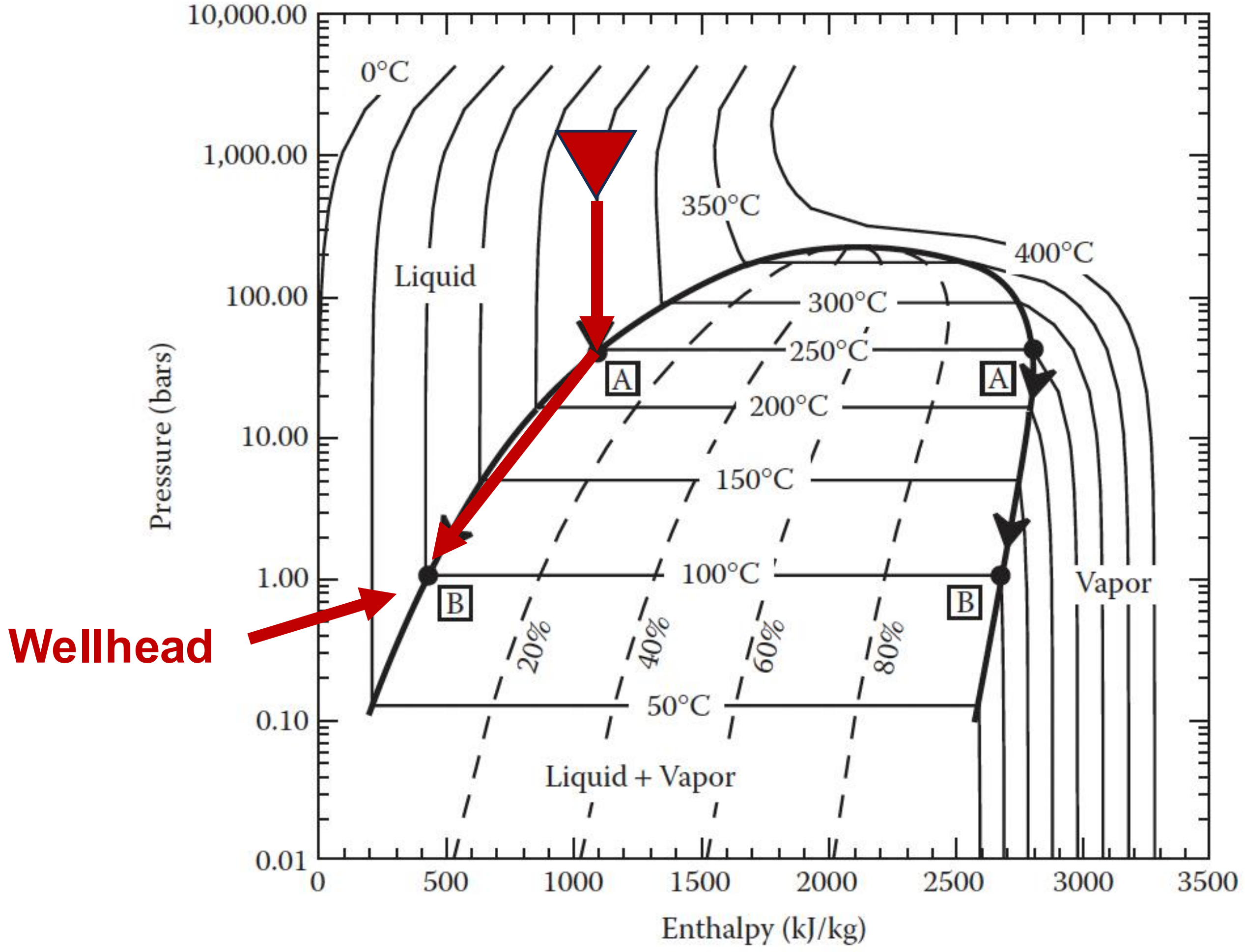


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure–enthalpy path followed by a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

Start: 250°C and 1000 bars.

H_l = 1113 J/gm

What happens as the fluid continues to ascend?

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

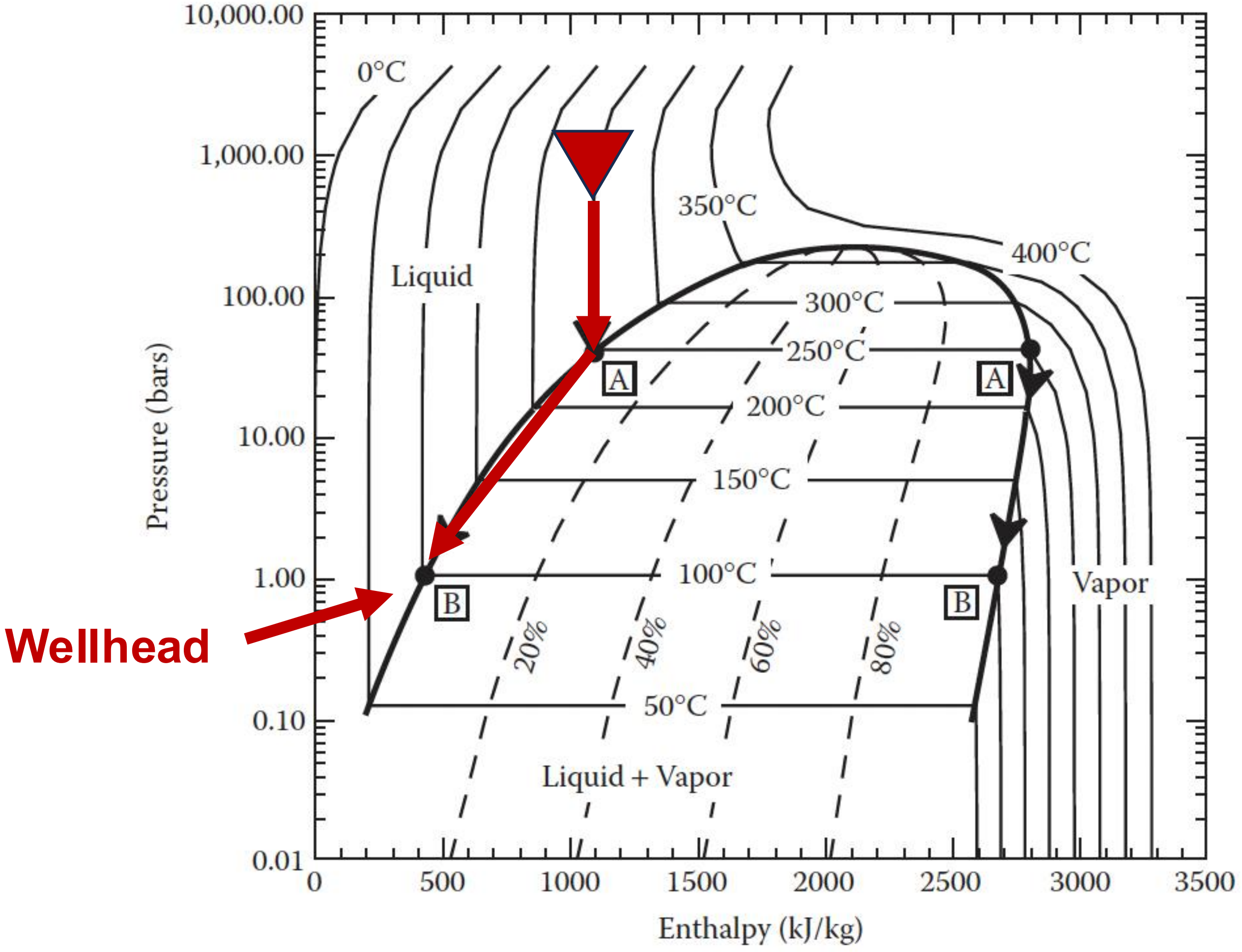


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure–enthalpy path followed by a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

Start: 250°C and 1000 bars.

H_l = 1113 J/gm

What is the proportion of liquid and steam that exits the wellhead, if the wellhead temperature is 100°C?

Source: Glassley, W. E., *Geothermal Energy*

Case Study: Thermodynamic properties of water

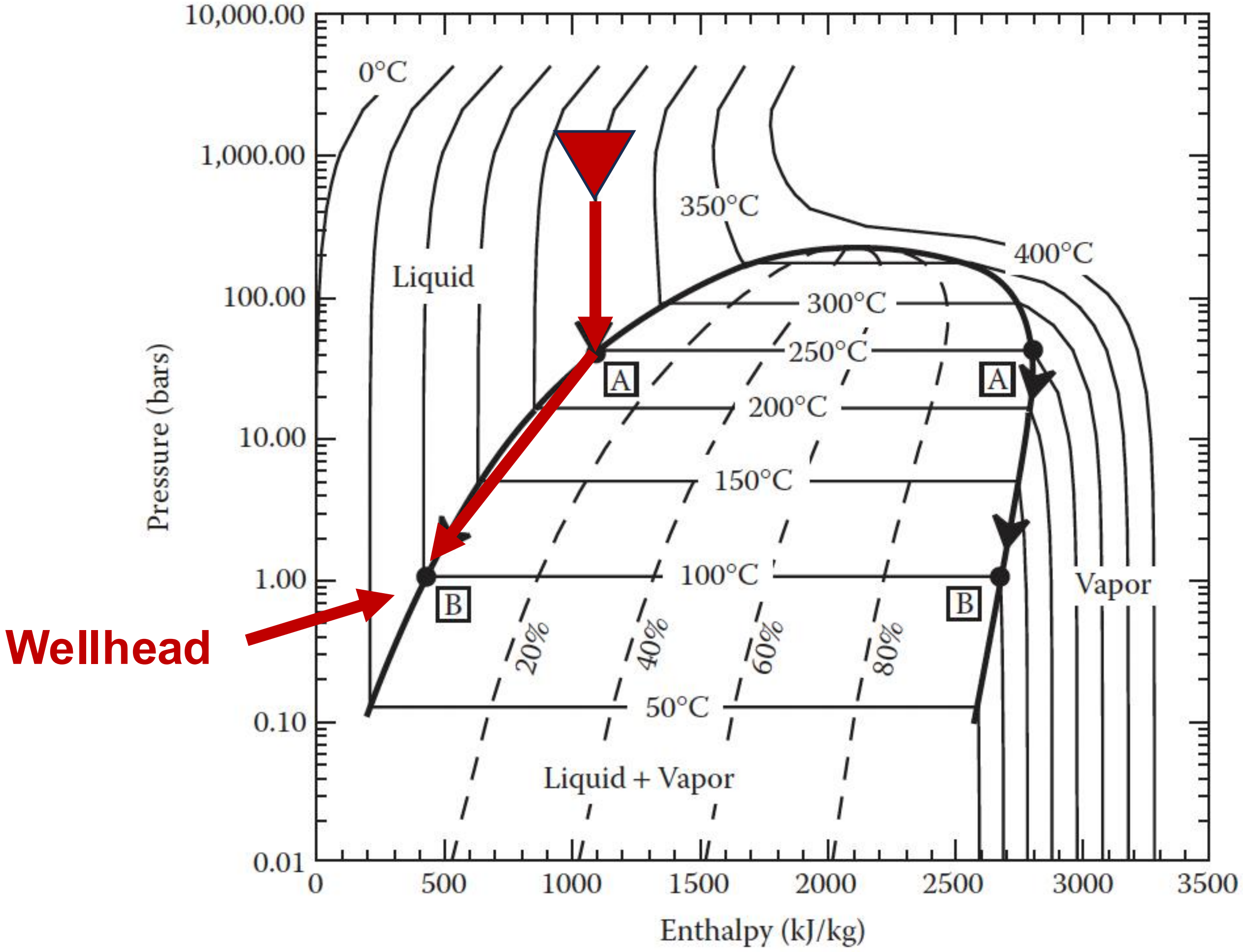


FIGURE 3.9 Pressure versus enthalpy diagram, contoured for temperature. The heavy black line encloses the region where steam and liquid coexist. The dashed lines are lines of constant mass percent steam coexisting with liquid water. The arrowed paths indicate the pressure–enthalpy path followed by a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

Start: 250°C and 1000 bars.

H_l = 1113 J/gm

What is the proportion of liquid and steam that exits the wellhead, if the wellhead temperature is 100°C?

Recall:

$H_{l,100°C}$ = 419 J/gm and $H_{v,100°C}$ = 2676 J/gm

Source: Glassley, W. E., *Geothermal Energy*