

Preparing for the Physics GRE: Day 3 Thermodynamics

Daniel T. Citron

dtc65@cornell.edu

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<http://greprep.dtcitron.com>

Heat Exchange

- Heat is energy exchanged between the system and the reservoir it is coupled to
 - Heat has units of energy: $[Q] = \text{J}$
 - Temperature is a completely different parameter
 - Heat capacity is the amount of energy required to raise the system temperature: $[C] = \text{J/K}$
14. Two identical 1.0-kilogram blocks of copper metal, one initially at a temperature $T_1 = 0^\circ \text{C}$ and the other initially at a temperature $T_2 = 100^\circ \text{C}$, are enclosed in a perfectly insulating container. The two blocks are initially separated. When the blocks are placed in contact, they come to equilibrium at a final temperature T_f . The amount of heat exchanged between the two blocks in this process is equal to which of the following? (The specific heat of copper metal is equal to 0.1 kilocalorie/kilogram $^\circ\text{K}$.)
- (A) 50 kcal
 - (B) 25 kcal
 - (C) 10 kcal
 - (D) 5 kcal
 - (E) 1 kcal

1st Law of Thermodynamics

- Equivalent to Conservation of Energy:
 - Change in system internal energy is equal to the heat input minus the work done by the system:

$$dU = dQ - dW$$

- Heat exchange definition: $dQ = TdS$
- Work done by the system on surroundings: $dW = - \vec{J} \cdot \vec{dx}$
 - J and x are “conjugate variables” with $[Jx] = \text{Energy}$
 - J is generalized force, x is generalized displacement
 - Ex: P and V; μ and N; H and M
- So the 1st law becomes $dU = TdS + \vec{J} \cdot \vec{dx}$
- Example:
 - Ideal gas in contact with heat bath and particle reservoir:

$$dU = TdS + PdV + \mu dN$$

1st Law: Manipulating Differentials

- The trick for many problems is manipulating differentials
- (Probably do not need to memorize all the Maxwell relations)
- Use dimensional analysis
- Check: what are you keeping constant?

- For example, use the first law to recover the formal definition of temperature

$$dU = TdS + PdV + \mu dN$$

66. For a system in which the number of particles is fixed, the reciprocal of the Kelvin temperature T is given by which of the following derivatives? (Let P = pressure, V = volume, S = entropy, and U = internal energy.)

(A) $\left(\frac{\partial P}{\partial V}\right)_S$

(B) $\left(\frac{\partial P}{\partial S}\right)_V$

(C) $\left(\frac{\partial S}{\partial P}\right)_U$

(D) $\left(\frac{\partial V}{\partial P}\right)_U$

(E) $\left(\frac{\partial S}{\partial U}\right)_V$

1st Law: Manipulating Differentials

- Another example: what is the difference between heat capacities C_p and C_v ?

14. For an ideal gas, the specific heat at constant pressure C_p is greater than the specific heat at constant volume C_v because the
- (A) gas does work on its environment when its pressure remains constant while its temperature is increased
 - (B) heat input per degree increase in temperature is the same in processes for which either the pressure or the volume is kept constant
 - (C) pressure of the gas remains constant when its temperature remains constant
 - (D) increase in the gas's internal energy is greater when the pressure remains constant than when the volume remains constant
 - (E) heat needed is greater when the volume remains constant than when the pressure remains constant

$$dU = dQ + PdV$$

$$PV = nRT$$

1st Law: Manipulating Differentials

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$$dU = dQ + PdV$$

$$PV = nRT$$

- Holding V constant, $dV = 0$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \frac{\partial Q}{\partial T}$$

- Holding P constant, there's an extra term from $PdV \neq 0$

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p = \frac{\partial Q}{\partial T} + P \frac{\partial V}{\partial T} = C_v + nR > C_v$$

- From intuition:
 - (B): this would mean $C_p = C_v$
 - (C): ?
 - (D): ideal gas energy depends on T only
 - (E): (begging the question)

1st Law: Ideal Gas Processes

- Isotherms in P-V state space
 - Holding T constant, the Ideal Gas Law tells us $PV = \text{Constant}$
- Adiabats in P-V state space
 - Integrate: $nC_V dT = -PdV = nRTdV/V$
 - We use $\gamma = C_P/C_V$
 - $\Rightarrow PV^\gamma = \text{Constant}$

- An example problem:

6. An ideal monatomic gas expands quasi-statically to twice its volume. If the process is isothermal, the work done by the gas is W_i . If the process is adiabatic, the work done by the gas is W_a . Which of the following is true?

- (A) $W_i = W_a$
- (B) $0 = W_i < W_a$
- (C) $0 < W_i < W_a$
- (D) $0 = W_a < W_i$
- (E) $0 < W_a < W_i$

(An additional example)

73. The adiabatic expansion of an ideal gas is described by the equation $PV^\gamma = C$, where γ and C are constants. The work done by the gas in expanding adiabatically from the state (V_i, P_i) to (V_f, P_f) is equal to

- (A) $P_f V_f$
- (B) $\frac{(P_i + P_f)}{2} (V_f - V_i)$
- (C) $\frac{P_f V_f - P_i V_i}{1 - \gamma}$
- (D) $\frac{P_i (V_f^{1+\gamma} - V_i^{1+\gamma})}{1 + \gamma}$
- (E) $\frac{P_f (V_f^{1-\gamma} - V_i^{1-\gamma})}{1 + \gamma}$

1st Law: Ideal Gas Processes

6. An ideal monatomic gas expands quasi-statically to twice its volume. If the process is isothermal, the work done by the gas is W_i . If the process is adiabatic, the work done by the gas is W_a . Which of the following is true?

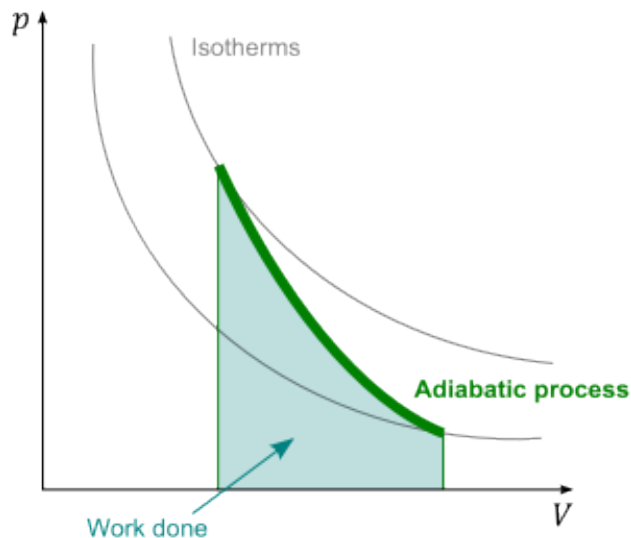
- (A) $W_i = W_a$
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- (D) $0 = W_a < W_i$
- (E) $0 < W_a < W_i$

- Isotherms: $PV = \text{Constant}$

$$W = \int P dV = \int \frac{nrT}{V} dV = nrT \log 2$$

- Adiabats: $PV^\gamma = \text{Constant}$

$$W = \int P dV = \int \frac{C}{V^\gamma} dV = \frac{C}{1-\gamma} V^\gamma (2^\gamma - 1) \approx .55nRT$$



Ideal Gas Processes $PV=nRT$

- Isochoric: V is constant $dV = 0$
- Isobaric: P is constant $dP = 0$
- Isothermal: T is constant $dT = 0$
- Adiabatic: no heat exchange $dQ = 0$
- **NB:** U of an *ideal* gas depends only on temperature

$$C_v = \frac{\partial Q}{\partial T} \Rightarrow \Delta Q = nC_v \Delta T$$

Process	ΔQ	ΔW	$\Delta U = \Delta Q - \Delta W$
Isochoric	$nC_v \Delta T$	0	$nC_v \Delta T$
Isobaric	$nC_p \Delta T$	$P \Delta V = nR \Delta T$	$nC_p \Delta T - nR \Delta T = nC_v \Delta T$
Isothermal	$Q = W = nRT \log(V_2/V_1)$	$nRT \log(V_2/V_1)$	0, $\Delta U \sim \Delta T$
Adiabatic	0	$\Delta U = -\Delta W = -nC_v \Delta T$	$nC_v \Delta T$

Entropy in Thermodynamics

- Formal definition of temperature given by the following (at equilibrium, holding all other parameters constant)

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

- Recall: relation between heat exchange and entropy

$$dQ = TdS$$

74. A body of mass m with specific heat C at temperature 500 K is brought into contact with an identical body at temperature 100 K, and the two are isolated from their surroundings. The change in entropy of the system is equal to

- (A) $(4/3)mC$
- (B) $mC \ln(9/5)$
- (C) $mC \ln(3)$
- (D) $-mC \ln(5/3)$
- (E) 0

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- What is the change in heat?

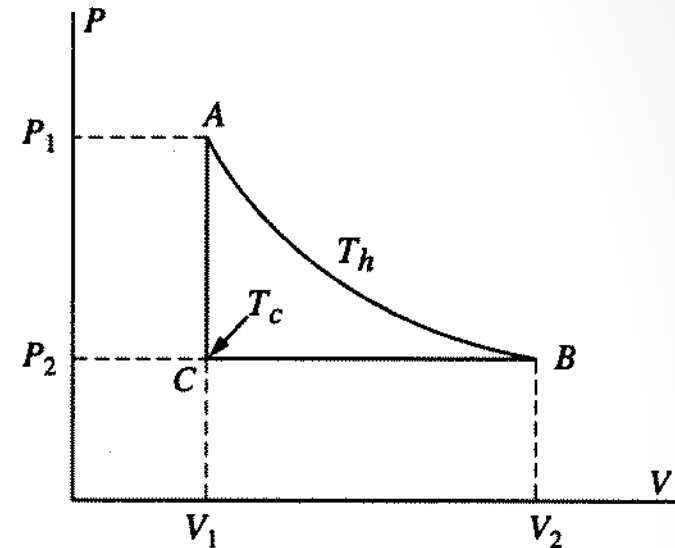
$$dQ = mCdT$$

- What is the *total* change in entropy?

$$\begin{aligned} dS &= \int \frac{dQ}{T} = \int \frac{mCdT}{T} \\ dS_1 + dS_2 &= \int_{100}^{300} \frac{mCdT}{T} + \int_{500}^{300} \frac{mCdT}{T} \\ &= mC(\log 3 - \log \frac{5}{3}) \end{aligned}$$

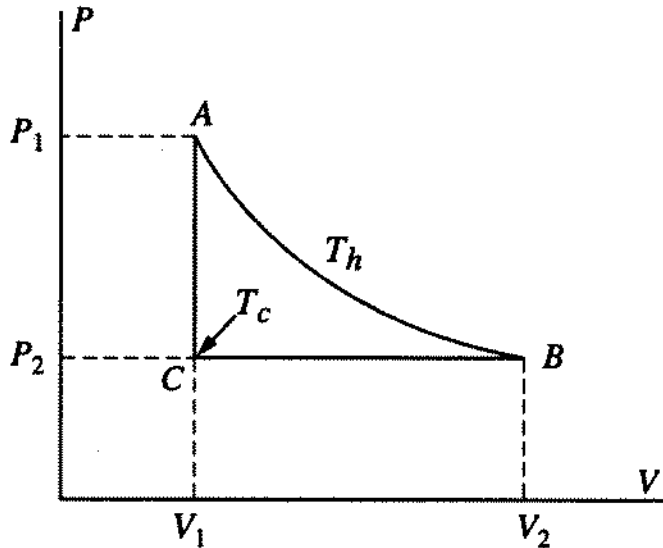
Engine Cycles

- Imagine a box of gas subject to a series of changes in pressure, temperature, volume, etc
- Draw the series of changes as a trajectory in the P-V plane
- Gas internal energy depends on T only:
 - If it returns to original state, no net change in energy
- Work done is the area enclosed by the cycle
 - Heat exchange with environment = Work done



15. Suppose one mole of an ideal gas undergoes the reversible cycle $ABCA$ shown in the P - V diagram above, where AB is an isotherm. The molar heat capacities are C_p at constant pressure and C_v at constant volume. The net heat added to the gas during the cycle is equal to
- (A) $RT_h V_2/V_1$
 - (B) $-C_p(T_h - T_c)$
 - (C) $C_v(T_h - T_c)$
 - (D) $RT_h \ln V_2/V_1 - C_p(T_h - T_c)$
 - (E) $RT_h \ln V_2/V_1 - R(T_h - T_c)$

Engine Cycles



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- Total change in energy during one cycle?
- Use 1st Law: $Q = W$
- Area under isotherm:

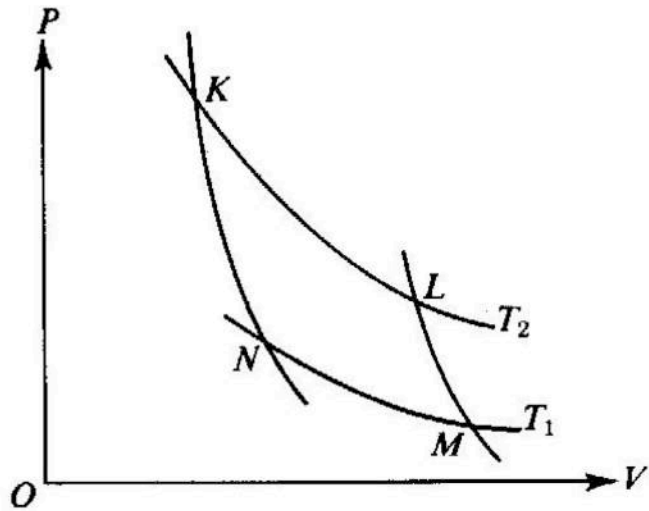
$$\int_{P_1}^{P_2} P dV = \int_{V_1}^{V_2} RT_h \frac{dV}{V} = RT_h \log \frac{V_2}{V_1}$$

- Area under isobar:

$$P_2(V_2 - V_1) = R(T_h - T_c)$$

- Subtract to find net work done and net heat exchange

Engine Cycles - Efficiency



- Engine efficiency = (work done by the system during one cycle)/(heat extracted from the hot reservoir)

- $e = W_{\text{cycle}}/|Q_H|$

- Carnot cycle: $e_{\text{Carnot}} = 1 - T_C/T_H$

- Carnot cycle

- Most efficient possible engine cycle
- Zero entropy change

95. In the cycle shown above, *KL* and *NM* represent isotherms, while *KN* and *LM* represent reversible adiabats. A system is carried through the Carnot cycle *KLMN*, taking in heat Q_2 from the hot reservoir T_2 and releasing heat Q_1 to the cold reservoir T_1 . All of the following statements are true EXCEPT:

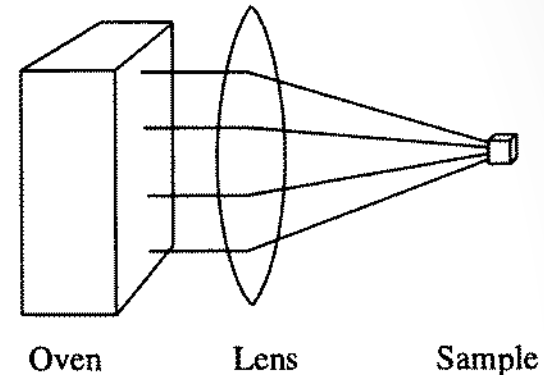
- (A) $Q_1/T_1 = Q_2/T_2$.
- (B) The entropy of the hot reservoir decreases.
- (C) The entropy of the system increases.
- (D) The work W done is equal to the net heat absorbed, $Q_2 - Q_1$.
- (E) The efficiency of the cycle is independent of the working substance.

16. An engine absorbs heat at a temperature of 727°C and exhausts heat at a temperature of 527°C . If the engine operates at maximum possible efficiency, for 2000 joules of heat input the amount of work the engine performs is most nearly

- (A) 400 J
- (B) 1450 J
- (C) 1600 J
- (D) 2000 J
- (E) 2760 J

2nd Law of Thermodynamics

- Many ways to state:
 - Work must be done to transfer heat from a colder body to a hotter body
 - Heat energy cannot be converted into work with perfect efficiency
 - For any thermodynamic process, the net change in entropy must be greater than or equal to zero
 - Colloquially, “entropy always increases”



91. An experimenter needs to heat a small sample to 900 K, but the only available oven has a maximum temperature of 600 K. Could the experimenter heat the sample to 900 K by using a large lens to concentrate the radiation from the oven onto the sample, as shown above?
- (A) Yes, if the volume of the oven is at least $\frac{3}{2}$ the volume of the sample.
 - (B) Yes, if the area of the front of the oven is at least $\frac{3}{2}$ the area of the front of the sample.
 - (C) Yes, if the sample is placed at the focal point of the lens.
 - (D) No, because it would violate conservation of energy.
 - (E) No, because it would violate the second law of thermodynamics.

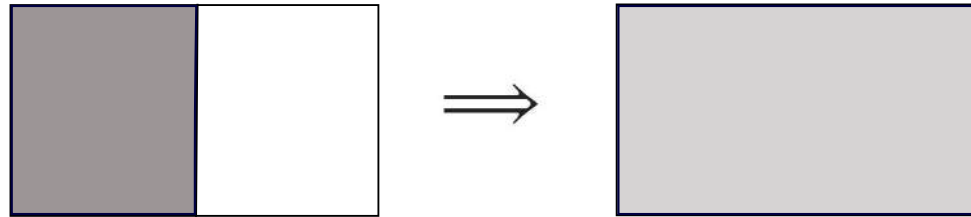
3rd Law of Thermodynamics

- Cannot cool system to 0 K in a finite number of steps
- Nernst's Theorem:
 - At 0 temperature, any system's entropy is 0. We take this to be a universal constant.
 - (Experimentally verified as well)

$$\lim_{T \rightarrow 0} S(\vec{X}, T) = 0$$

Free Expansion of Ideal Gas

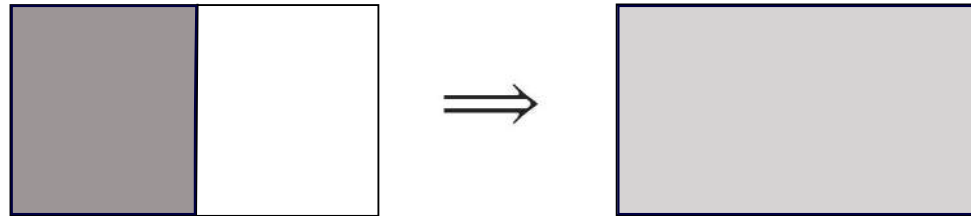
- N molecules of an ideal gas all occupy the left half of a thermally insulated box, while the right half is empty
- We remove the barrier and allow the gas to fill the whole box



- What happens to the gas's temperature?
- What happens to the gas's entropy?

Free Expansion of Ideal Gas

- N molecules of an ideal gas all occupy the left half of a thermally insulated box, while the right half is empty
- We remove the barrier and allow the gas to fill the whole box



- What happens to the gas's temperature?
 - Stays constant
 - Microscopically, no change in kinetic energy of the gas molecules
 - Macroscopically, $U = U(T)$ for ideal gas, and U does not change
- What happens to the gas's entropy?
 - Increases
 - Free expansion is a spontaneous and irreversible process
 - Entropy is extensive

Van der Waals Gas

- Real gas molecules locally repel one another
- Van der Waals proposed new model that accounted for excluded volume of molecules
- New parameters:
 - a: intermolecular attraction
 - b: excluded volume
- Less accurate at lower T
 - Predicts *negative* dV/dP

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

79. Consider 1 mole of a real gas that obeys the van der Waals equation of state shown above. If the gas undergoes an isothermal expansion at temperature T_0 from volume V_1 to volume V_2 , which of the following gives the work done by the gas?

(A) 0

(B) $RT_0 \ln\left(\frac{V_2}{V_1}\right)$

(C) $RT_0 \ln\left(\frac{V_2 - b}{V_1 - b}\right)$

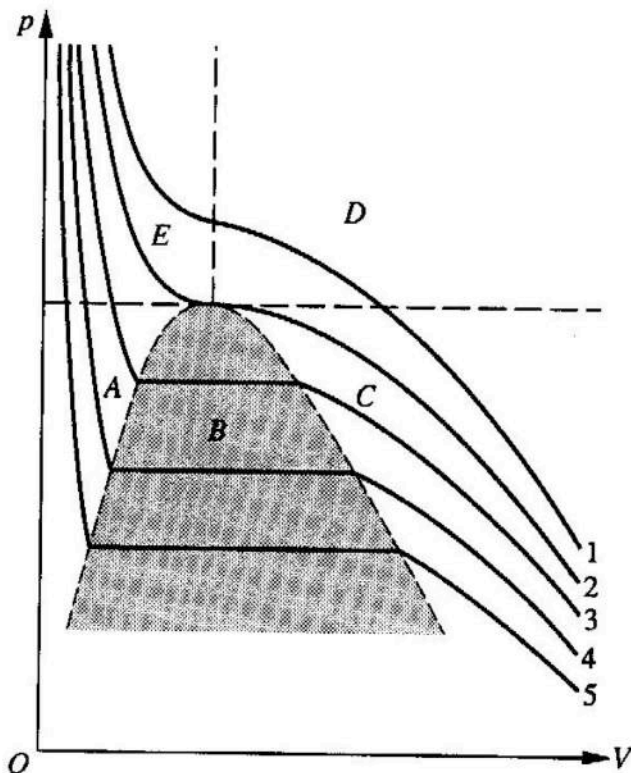
(D) $RT_0 \ln\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

(E) $RT_0\left(\frac{1}{(V_2 - b)^2} - \frac{1}{(V_1 - b)^2}\right) + a\left(\frac{1}{V_2^3} - \frac{1}{V_1^3}\right)$

Phase Transitions

- A qualitative change in the properties of matter
 - Liquid-solid, gas-liquid, paramagnet-ferromagnet
- (More abstractly, change in system symmetries)
- Example below
 - Phase diagram for liquid-gas transition in VDW gas

Questions 46-47



Isotherms and coexistence curves are shown in the pV diagram above for a liquid-gas system. The dashed lines are the boundaries of the labeled regions.

46. Which numbered curve is the critical isotherm?

- (A) 1
- (B) 2
- (C) 3
- (D) 4
- (E) 5

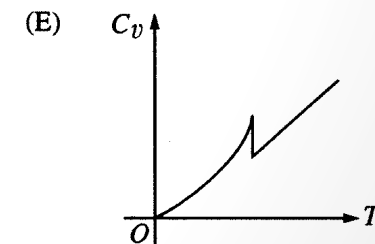
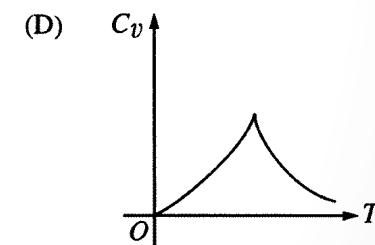
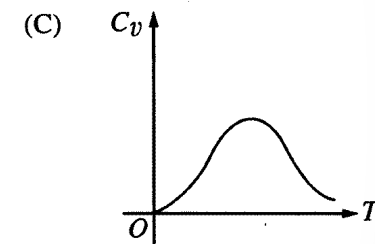
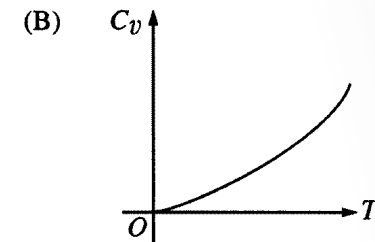
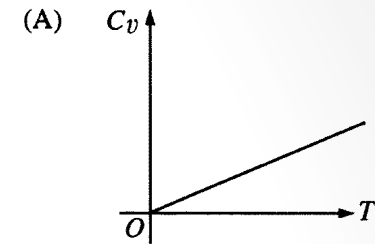
47. In which region are the liquid and the vapor in equilibrium with each other?

- (A) A
- (B) B
- (C) C
- (D) D
- (E) E

Phase Transitions

- Some phase transitions are characterized by divergences in measurable properties
- 1st order transition:
 - Sudden discontinuous change in system properties
- 2nd order transition:
 - Continuous change in system properties
 - Discontinuity in derivative

95. Which of the following curves is characteristic of the specific heat C_v of a metal such as lead, tin, or aluminum in the temperature region where it becomes superconducting?



Thermodynamics Summary

- 1st Law of Thermodynamics
 - Manipulating Differentials
 - Ideal Gas Processes
 - Engine Cycles
- 2nd Law of Thermodynamics
 - Entropy
- Additional Topics
 - **Thermodynamic potentials** – Gibbs, Enthalpy, Helmholtz
 - Engine efficiency
 - 3rd Law of Thermodynamics
 - Van der Waals Gas
 - Phase Transitions