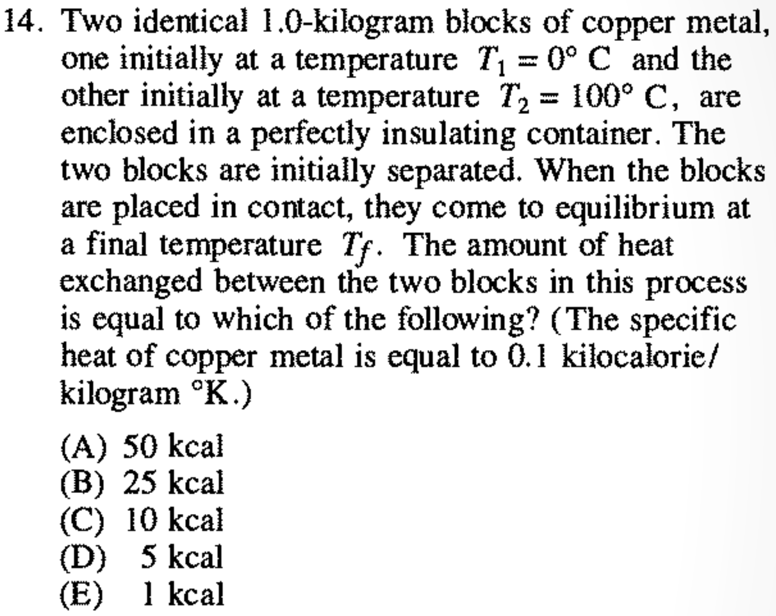
Thermodynamics Summary

- 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

Heat Exchange

- Heat is *energy* exchanged between the system and the reservoir it is coupled to
  - Heat has units of energy: [Q]= J
  - Temperature is a completely different parameter
- Heat capacity is the amount of energy required to raise the system temperature: [C] = J/K



14. Two identical 1.0-kilogram blocks of copper metal, one initially at a temperature $T_1 = 0°\ \text{C}$ and the other initially at a temperature $T_2 = 100°\ \text{C}$, 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 °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: $dW = -\vec{J} \cdot \overrightarrow{dx}$
  - J and x are "conjugate variables" with [Jx] = Energy
  - J is generalized force, x is generalized displacement
  - Ex: P and V; μ and N; H and M
- So the 1st law becomes $dU = TdS + \vec{J} \cdot \overrightarrow{dx}$
- Example:
  - Ideal gas in contact with heat bath and particle reservoir:

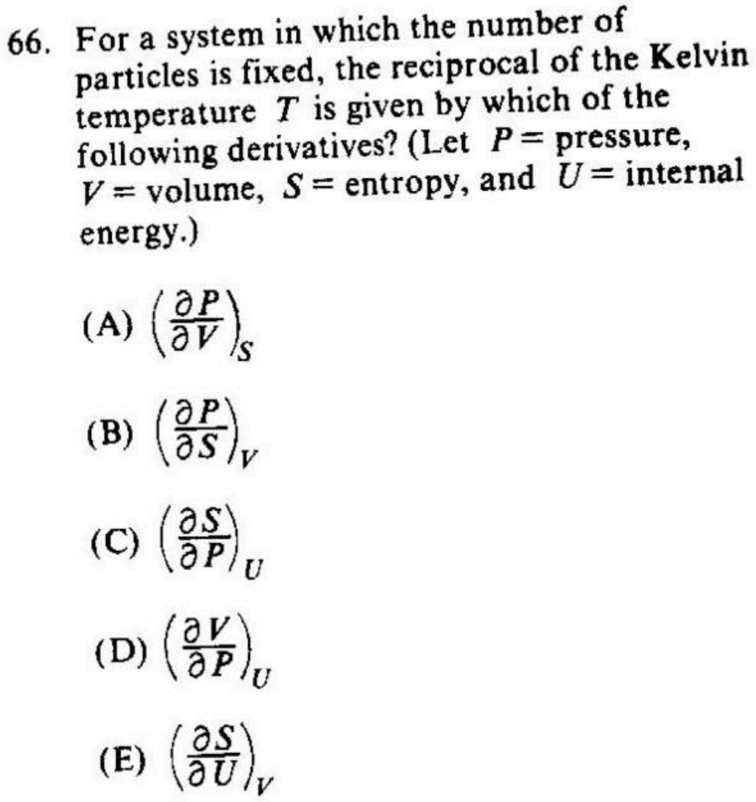
$$dU = TdS + PdV + \mu dN$$

1^{st} 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) $\left(\frac{\partial P}{\partial S}\right)_V$

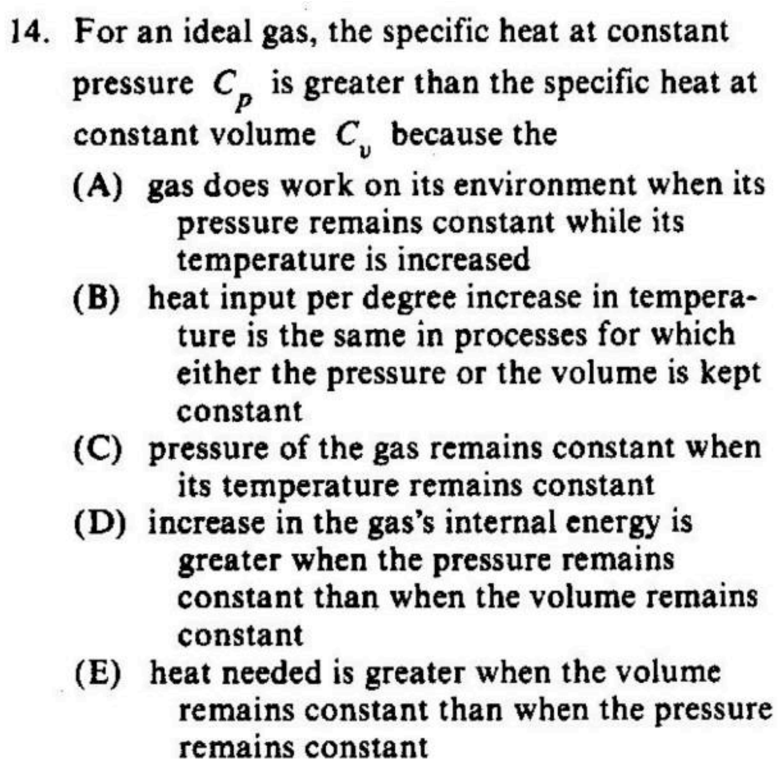
(C) $\left(\frac{\partial S}{\partial P}\right)_U$

(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

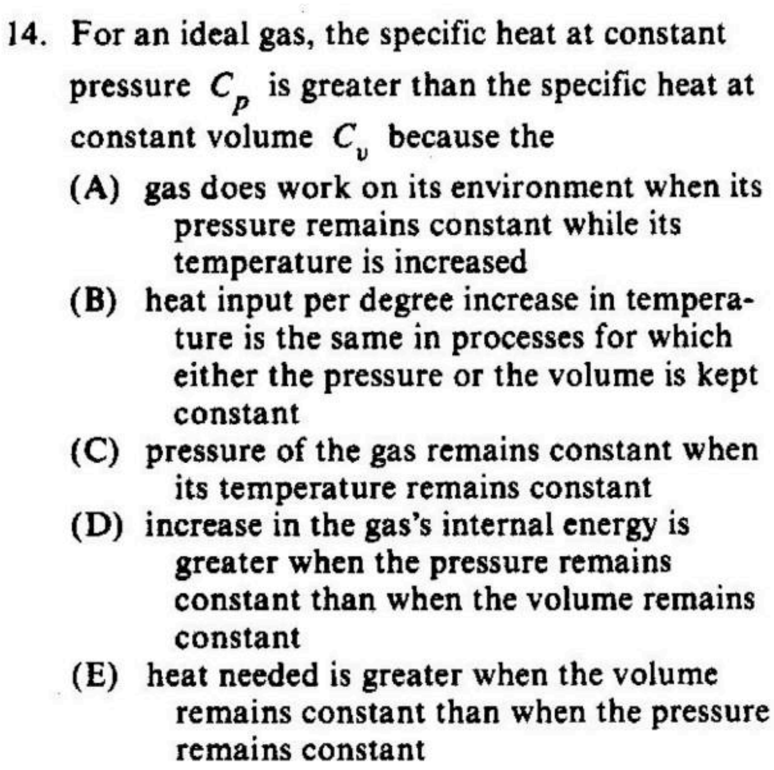
(C) pressure of the gas remains constant when its temperature remains constant

(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

$dU = dQ + PdV$ $\qquad\qquad$ $PV = nRT$

1^{st} 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 ≠ 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)

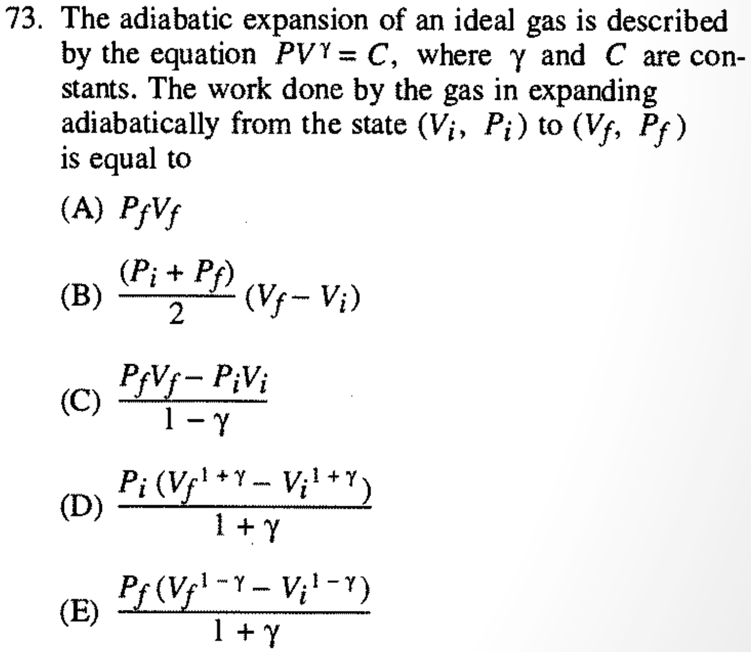
1st Law: Ideal Gas Processes

- Isotherms in P-V state space
  - Holding T constant, the Ideal Gas Law tells us PV = 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) $\dfrac{(P_i + P_f)}{2}(V_f - V_i)$
(C) $\dfrac{P_f V_f - P_i V_i}{1 - \gamma}$
(D) $\dfrac{P_i (V_f^{1+\gamma} - V_i^{1+\gamma})}{1 + \gamma}$
(E) $\dfrac{P_f (V_f^{1-\gamma} - V_i^{1-\gamma})}{1 + \gamma}$

1st Law: Ideal Gas Processes

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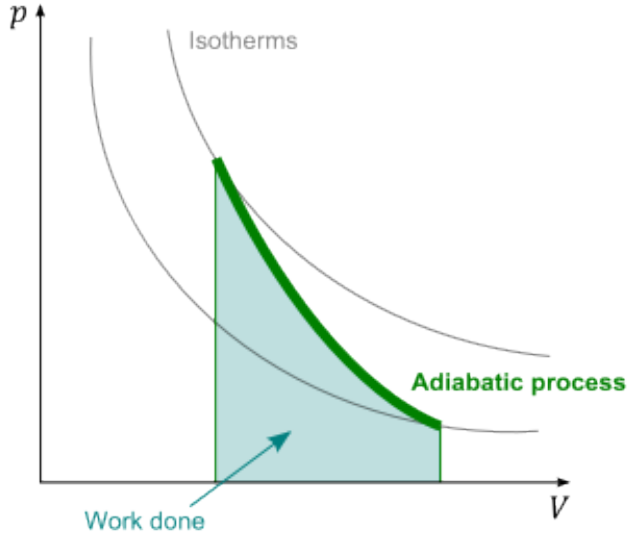
(C) $0 < W_i < W_a$
(D) $0 = W_a < W_i$
(E) $0 < W_a < W_i$

- Isotherms: PV = Constant

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

- Adiabats: PV^{γ} = Constant

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



http://www.physicsgrad.com/pgre/0177-6

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**	**ΔU=ΔQ-ΔW**
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	$\Delta U = -\Delta W$ $= - nC_V\Delta T$	$nC_V\Delta T$

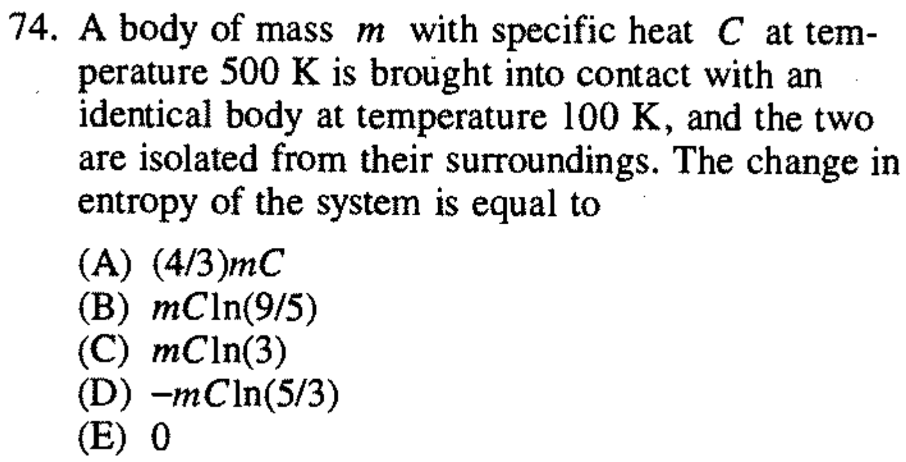
Entropy in Thermodynamics

- 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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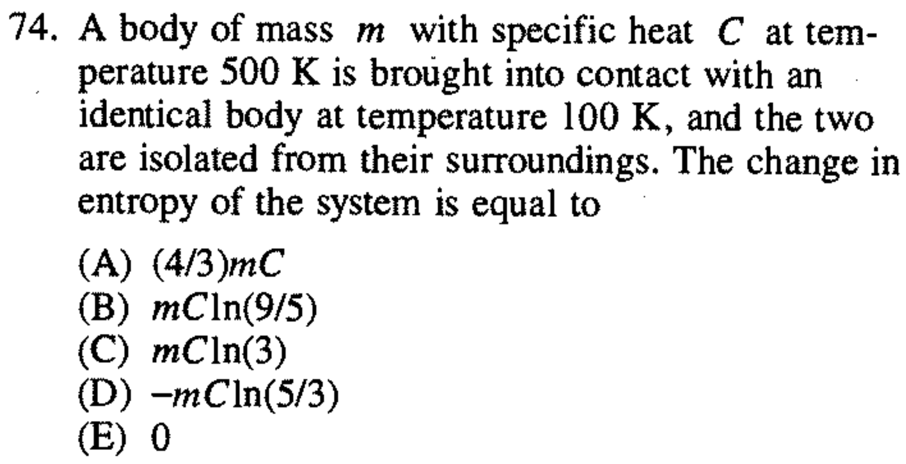

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(E) 0

- What is the change in heat?

$$dQ = mCdT$$

- What is the *total* change in entropy?

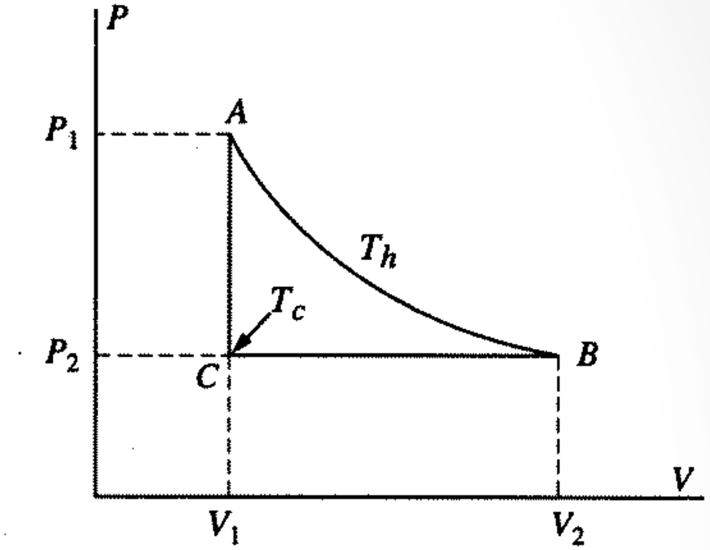
$$dS = \int \frac{dQ}{T} = \int \frac{mCdT}{T}$$

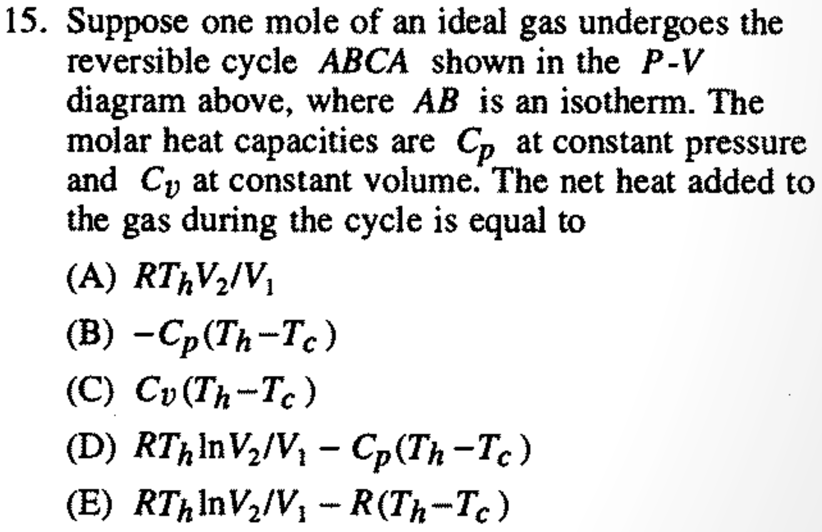
$$dS_1 + dS_2 = \int_{100}^{300} \frac{mCdT}{T} + \int_{500}^{300} \frac{mCdT}{T}$$

$$= mC(\log 3 - \log {}^{5}\!/_{3})$$

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_hV_2/V_1

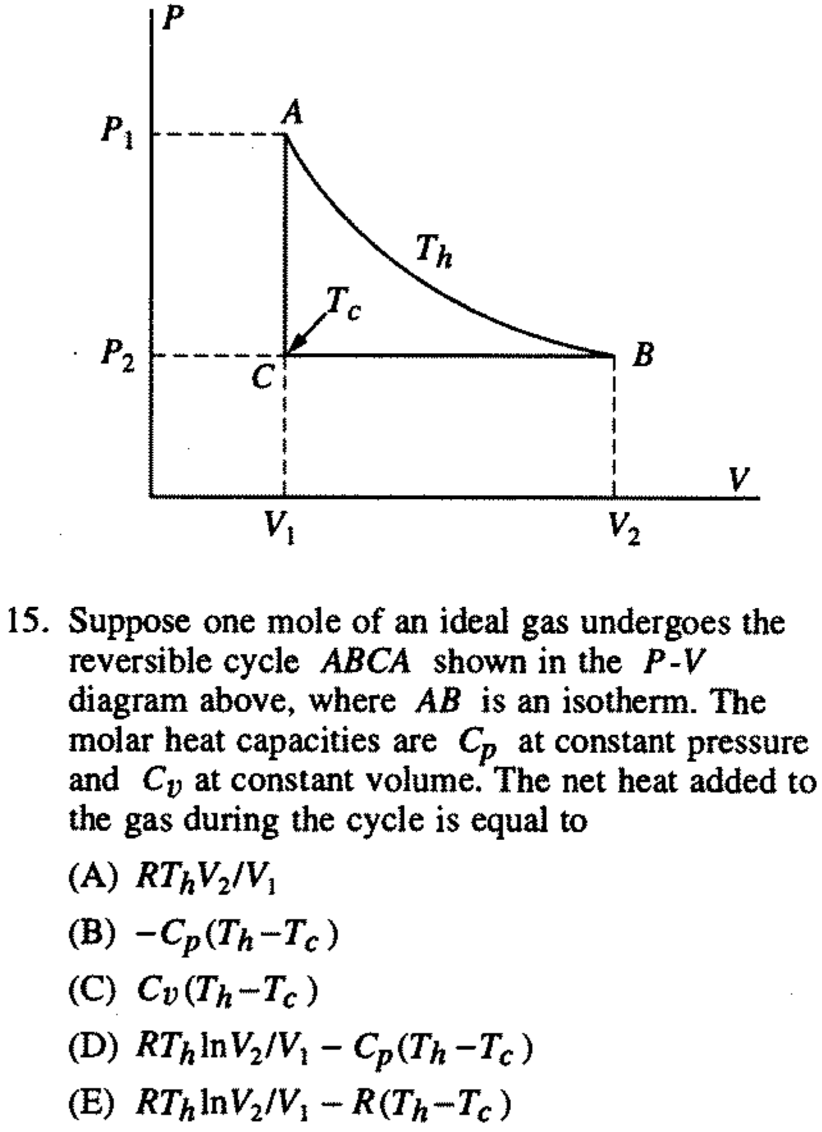
(B) $-C_p(T_h-T_c)$

(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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(D) $RT_h \ln V_2/V_1 - C_p(T_h - T_c)$

(E) $RT_h \ln V_2/V_1 - R(T_h - T_c)$

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

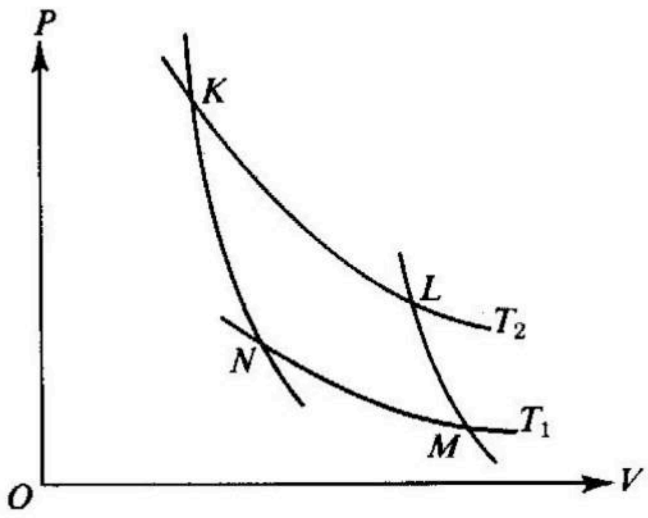
$$\int_{P_1}^{P_2} PdV = \int_{V_1}^{V_2} RT_h \frac{dV}{V} = RT_h \log\frac{V_2}{V_1}$$

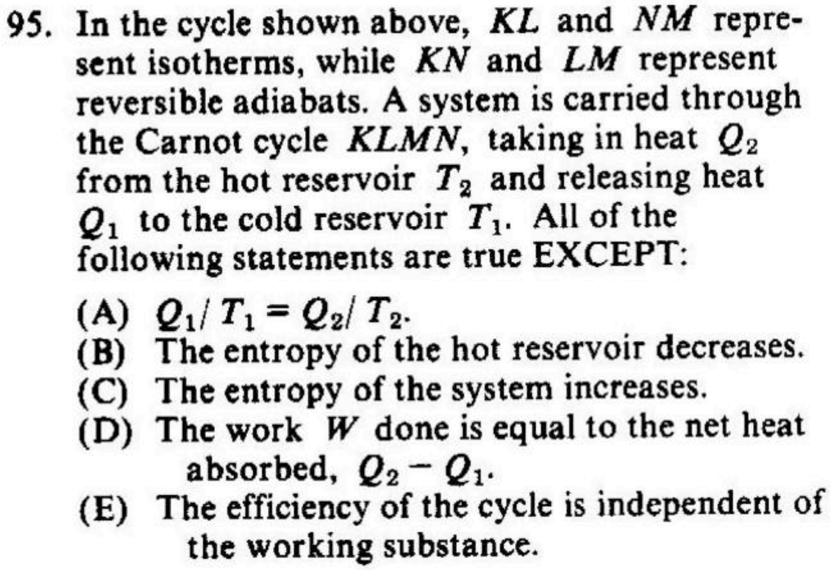
- Area under isobar:

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

- Subtract to find net work done and net heat exchange

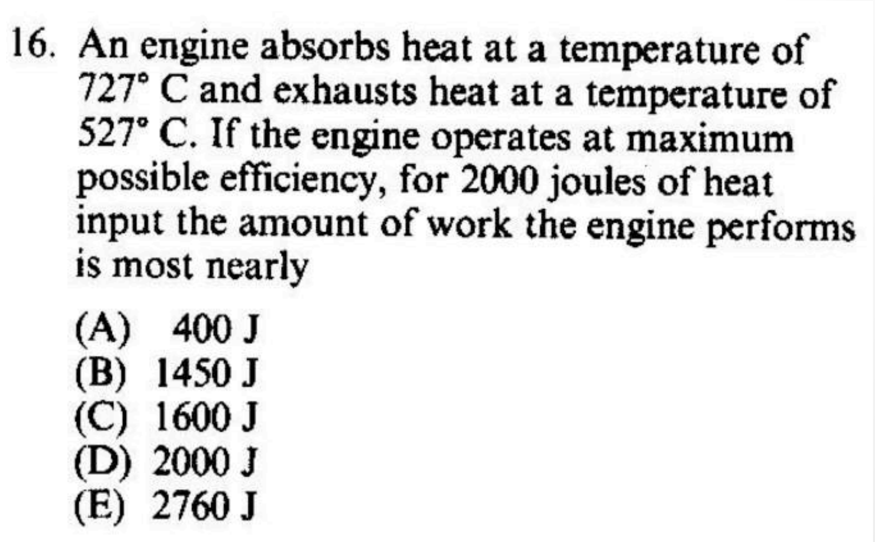
Engine Cycles - Efficiency




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.

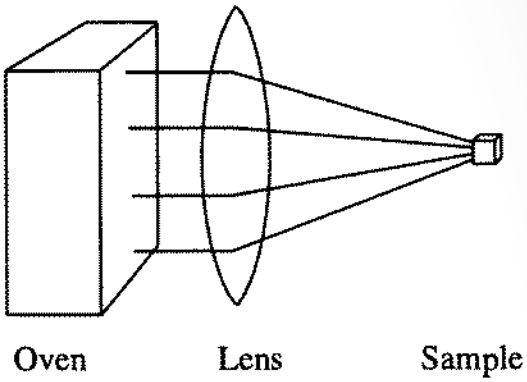
- Engine efficiency = (work done by the system during one cycle)/(heat extracted from the hot reservoir)
  - $e = W_{cycle}/|Q_H|$
  - Carnot cycle: $e_{Carnot} = 1 - T_C/T_H$
- Carnot cycle
  - Most efficient possible engine cycle
  - Zero entropy change


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 <u>cannot</u> 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 3/2 the volume of the sample.
(B) Yes, if the area of the front of the oven is at least 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.

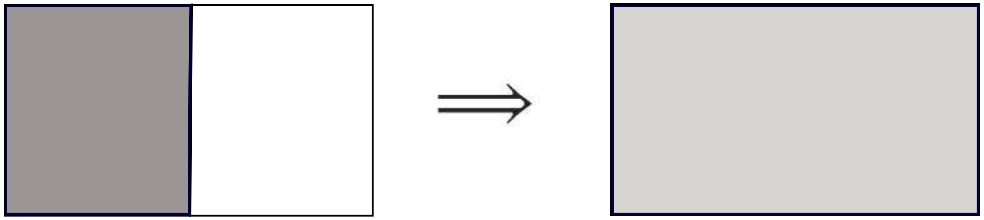
3rd Law of Thermodynamics

- 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)

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

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?

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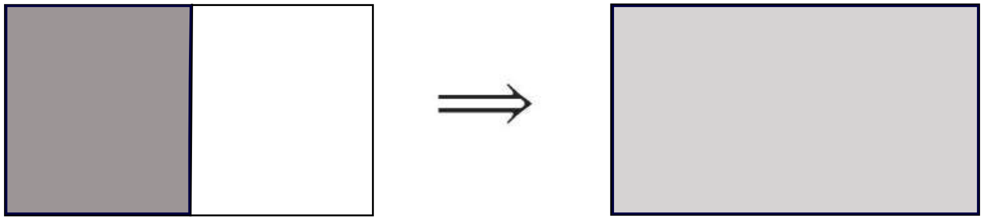
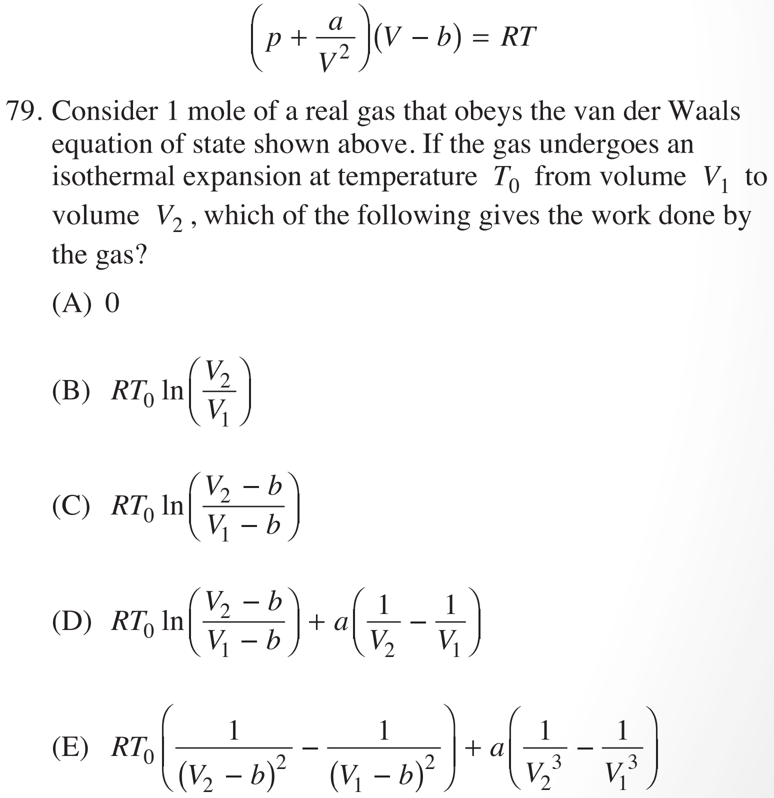


- What happens to the gas's temperature?
  - Stays constant
  - Microscopically, no change in kinetic energy of the gas molecules
  - Macroscopically, U = U(T) for ideal gas, and U does not change
- What happens to the gas's entropy?
  - Increases
  - Free expansion is a spontaneous and irreversible 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) $RT_0 \ln\left(\frac{V_2 - b}{V_1 - b}\right)$

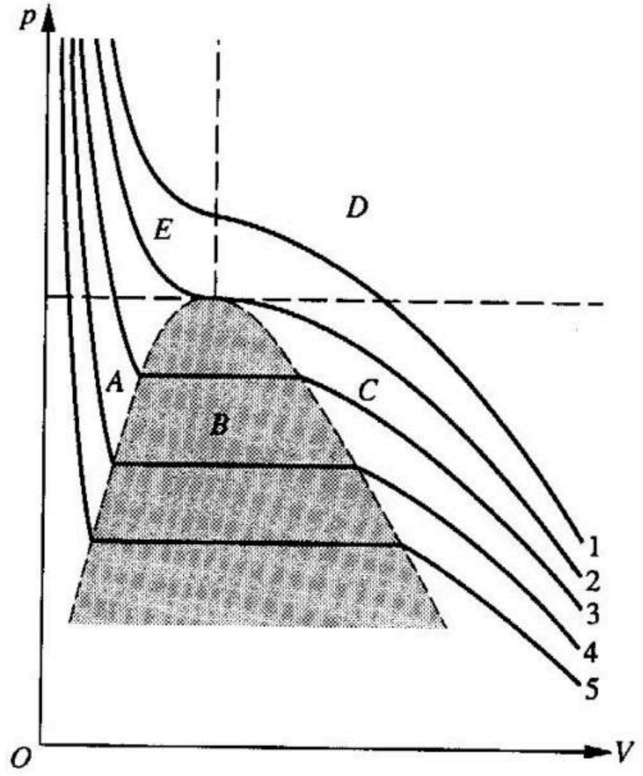
(D) $RT_0 \ln\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

(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?

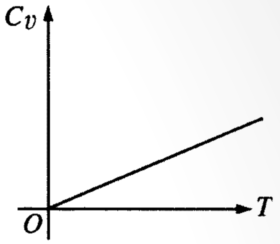
    (A) *A*
    (B) *B*
    (C) *C*
    (D) *D*
    (E) *E*

Phase Transitions

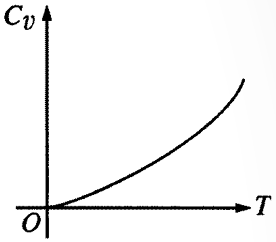
- Some phase transitions are characterized by divergences in measurable properties
- 1st order transition:
  - Sudden discontinuous change in system properties
- 2nd order transition:
  - Continuous change in system properties
  - Discontinuity in derivative

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?

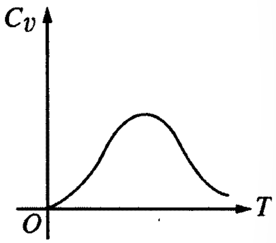
(A)



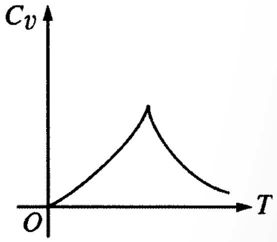
(B)



(C)



(D)



(E)